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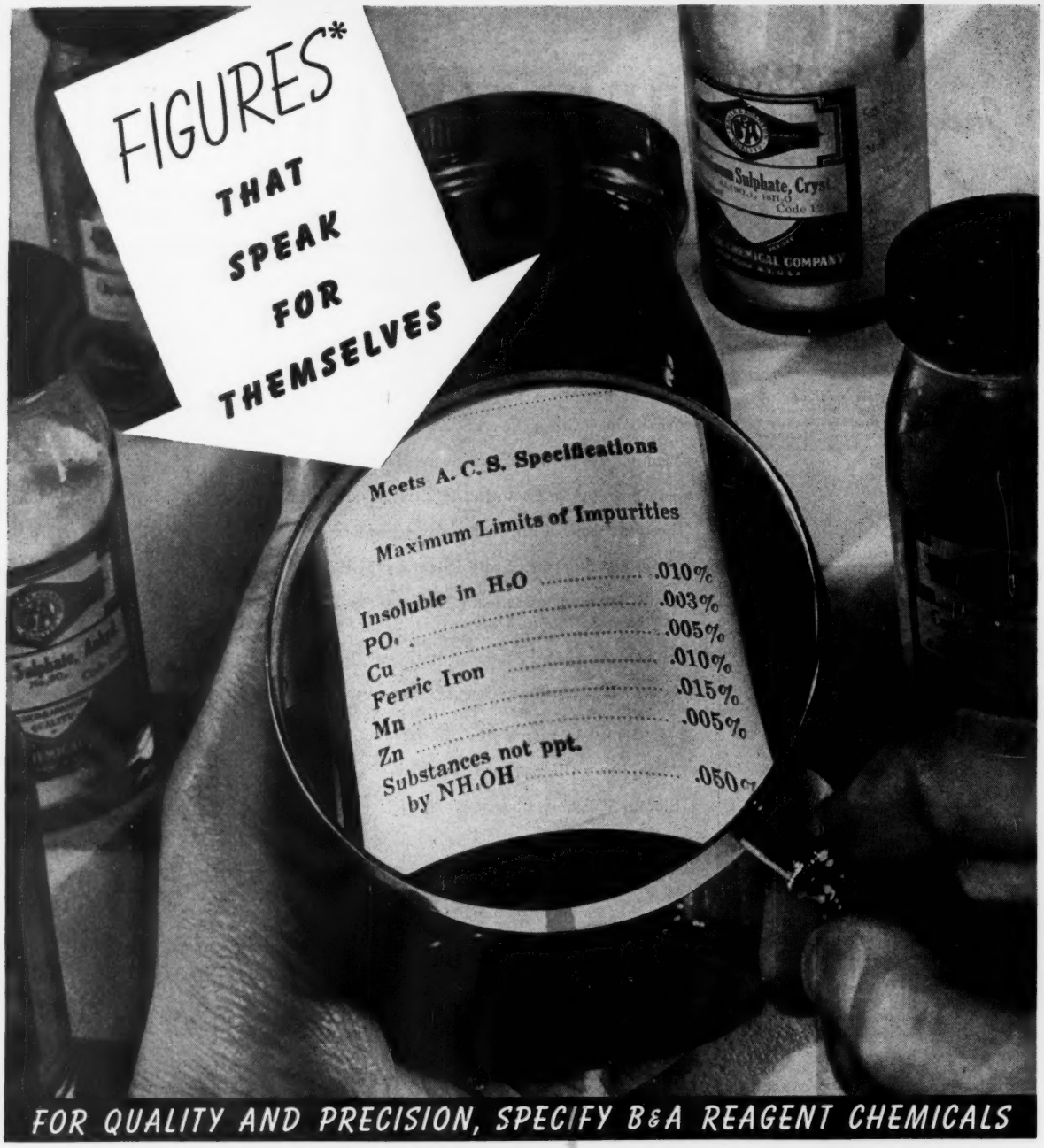

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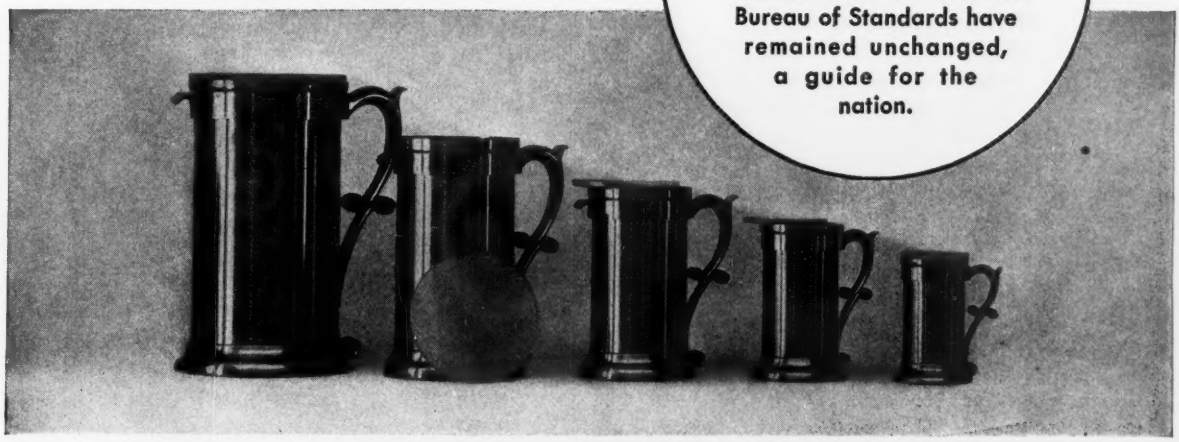

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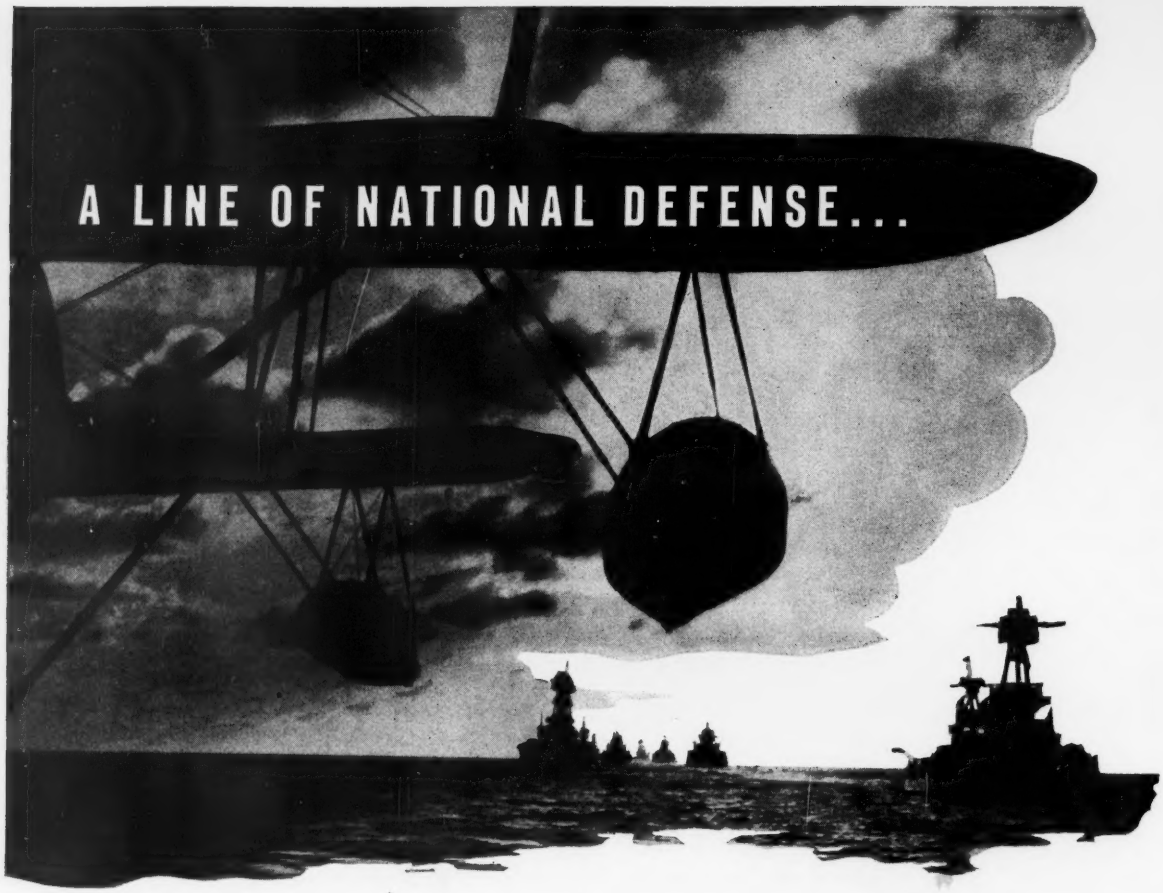

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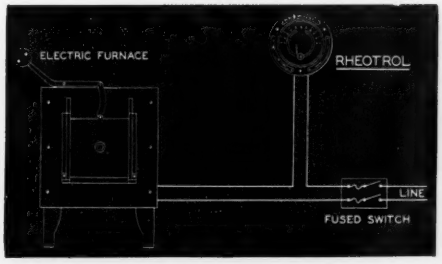

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(For biographical sketch of John Mercer, see page 80.)

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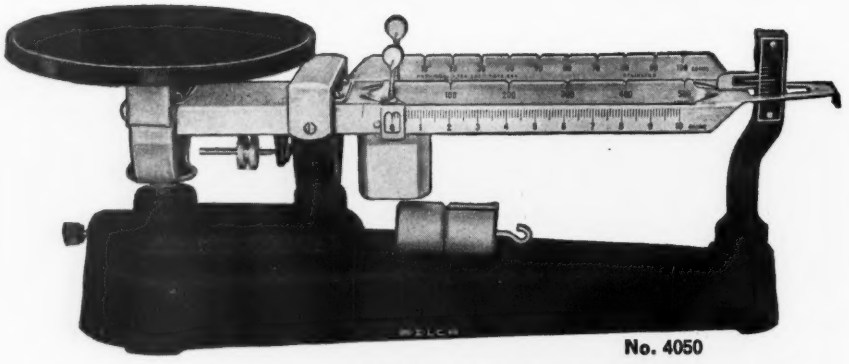

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Editor's Outlook

MAYBE we take too narrow a view of our responsibilities, we teachers. Perhaps we feel that just because we teach chemistry our main job is to train chemists. The trouble is partly that, being serious about our profession, we find our greatest interest in those students who are themselves most serious about it, particularly those who feel inspired actually to become chemists.

On the other hand we spend a good deal of energy "selling" our science to the layman, arguing to anyone who will listen that chemistry is one of the greatest contributors to modern life and progress. Although this recognizes the place that chemistry should occupy in one's general education, not nearly enough attention has been given to the needs of the non-professional student of chemistry. The committee report which appeared in the last number of the JOURNAL bears witness, however, to the increasing realization of these needs.

We submit that this is one of the large problems of chemical education: How much of what kind of chemistry should be taught to whom? Although we really haven't tried it, the answer is probably *not:* As much as possible of all kinds of chemistry to everybody. In our college courses we generally distinguish between the prospective chemists and the non-professional students; in the high school there is nearly the same relation between the "college preparatory" and the "general" courses.

The place of science in general and of chemistry in particular in the educational curriculum needs no defense. But there is certainly a growing feeling that the sort of chemistry which is necessary in the training of a professional chemist is not what the person needs who merely wants to establish a basis for the appreciation and evaluation of present and future science. But just what does he need?

"Consumer chemistry" is fast becoming a shibboleth. We have little use for shibboleths; they open doors, but so does a swift kick. However, we don't want to be dogmatic about it and would really like to know what it is all about. Some people think this is the answer.

Planning a course for the non-professional college student is a problem which can well challenge the intelligence and ingenuity of every teacher of chemistry. We would be less worried about the outcome, however, if we could banish the thought that, despite repeated denials, the general course will involve lower standards. Last month we advocated dropping outworn material from our courses; this month we feel like issuing a word of caution against going to the opposite extreme. Beware lest we cut out all the meat and serve nothing but gravy!

What has a student the right to expect from a "general course?" Above all, it seems, a glimpse of chemistry *as the chemist sees it;* not as the news reporter sees it, the butcher, the baker, the candlestick maker.

The danger is perhaps greater at the high-school level. We recently saw the results of a questionnaire which attempted to establish the desirable content of a "general" chemistry course in the high school. A large number of specific items of content were listed and a vote taken on each, to indicate whether or not it should be included in a general course. The amazing result was that ten out of the eleven items with the highest votes were precautions for keeping out of danger, from "properties and danger of carbon monoxide" to "dangers in the use of laxatives." At the other end of the scale the vote indicated that *nothing* should be included on "the hypotheses, theories, and laws of chemistry." This may be partly, but not entirely attributed to the fact that some answers to the questionnaire came from people who had little if any knowledge of chemistry.

We cannot see that any such negative treatment of the subject will leave the student with the remotest idea of what chemistry really is. Rather, we feel that the promise of hope lies in the committee report cited above. The result of this study shows that thoughtful teachers are aware of the problem and believe that a solution should be sought. Furthermore, that the objectives of the general course should be: to develop the ability to do critical thinking; to show how science has contributed to the solution of the problems of living; to familiarize students with the facts, principles, and concepts of chemistry. In the fulfilment of this last objective we believe that it is the eternal and inevitable responsibility of the individual teacher to decide what subject matter he can best use in carrying out the other objectives. No self-respecting teacher will try to avoid it by hiding behind a prepared "syllabus."

One of the authors of the above report has elaborated his views elsewhere[1] and we recommend his remarks to our readers. Particularly, we like his summary of the present situation in regard to the attempts which have been made to solve the general-course problem:

> "One needs all the optimism available, however, upon turning from the gratifying degree of recognition of a teaching problem to the measures that have been put into operation in the attempt to solve the problem. Not that there is any lack of such ventures. An annotated list prepared for the committee covered 35 single-spaced pages. It reminds one somewhat of the old expression about the man who mounted his horse and rode off in all directions at the same time. Unfortunately it seems to disclose a certain bankruptcy on the part of college teachers of science in the matter of a philosophy of the educational process. Until we can make up our collective mind on what we are trying to do with science as an element in general education at the college level we are not likely to do much of anything with it. We college teachers are inclined to be 'sniffy' about the doctrinaire attitudes of many leaders in secondary education toward the educational process. But with all their vagueness about 'functionalism,' the 'socialized curriculum' and all that, there is a nucleus of agreement among secondary-school teachers about what they are trying to accomplish which we college teachers may well envy."

[1] TAYLOR, "Science in general education at the college level," *Science Education*, **24**, 241 (Oct., 1940).

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What's Been Going On

THE National Chemical Exposition in Chicago, December 11–14, was a notable success; already space is reserved by many of the exhibitors for the next exposition in 1942. About 35,000 people attended, inspecting the 115 exhibitors' booths, in addition to several educational exhibits arranged under the direction of Mr. C. R. Moulton. Of particular interest was that demonstrating the application of light to industry.

The Industrial Motion Pictures were a feature in which both teachers and the general public showed great interest. The following pictures were shown in a program arranged by Arthur Guillaudeu:

1. "Approved by the Underwriters"—Underwriters' Laboratories, Inc. Protection of life and property by testing for safety.
2. "The Romance of Iron and Steel"—American Rolling Mill Co. From iron ore to finished sheets and strips.
3. "King Cotton"—General Motors Corporation. Growth of cotton; its uses, including fabrics, lacquers, plastics, highways.
4. "Manufacture of Pulp and Paper"—Rhinelander Paper Co. From the growing tree through the mill to the finished paper.
5. "Eyes of Science"—Bausch and Lomb Optical Co. Theory, manufacture, and application of modern optical instruments.
6. "Rubber Reborn"—Midwest Rubber Reclaiming Co. Reclaiming rubber from discarded articles for re-use.
7. "A Woolen Yarn"—General Electric Co. From shearing the sheep to manufacturing cloth.
8. "Norton Abrasives"—Norton Co. Manufacturer of grinding wheels.
9. "It Isn't Done with Mirrors"—American Cyanamid Co. Development and production of synthetic resins. Laboratory and plant scenes.
10. "Frontiers of the Future"—General Motors Corporation. An inspiring showing of some of the new horizons that lie before us.
11. "The Sugar Trail"—General Electric Co. Cultivation of sugar beets; harvesting; manufacture of sugar.
12. "A New World through Chemistry"—E. I. du Pont de Nemours and Co. Recent developments; nylon, neoprene, synthetic rubber, "lucite" plastic, cellulose.
13. "Modern Pyramids"—National Carbon Co., Inc. Manufacture of carbon brushes, as for motors, generators, etc.
14. "Making of Safety Glass"—Ford Motor Co. From raw materials to finished safety glass.
15. "Keeping Nature on Its Course"—Hiram Walker and Sons, Inc. Contrasting old and new methods of converting grain to whiskey.
16. "The Manufacture of Laboratory Glassware"—Corning Glass Works. Production of "pyrex" ware from raw batch to completed articles.
17. "Mining, Milling, Smelting, and Refining of Nickel"—International Nickel Co., Inc. From the mining of the ore to the finished products.
18. "Mining Lead"—Bureau of Mines, Pittsburgh.
19. "Milling, Smelting, and Refining Lead"—Bureau of Mines, Pittsburgh.
20. "Story of a Diatom"—Johns-Manville Co.

Four industrial chemical conferences were held during the afternoons and evenings while the exposition was in progress. The theme of the conferences was the application of chemistry to industry and commerce. The following papers were presented:

"New Developments in Synthetic Chemicals and Materials for Fuels and Lubricants," by Walter G. Whitman, Massachusetts Institute of Technology.

"New Developments in Synthetic Chemicals and Materials in the Rubber Industry," by Per K. Frolich, Standard Oil Development Company.

"The Influence of Electrolytic Processes on the Development of the Chemical Industries," by C. G. Fink, Columbia University.

"The Influence of New Solvents on the Development of the Chemical Industries," by C. L. Gabrial, Commercial Solvents Corporation.

"The Influence of the Friedel-Crafts Reaction on the Development of the Chemical Industries," by E. C. Britton, Director of Organic Research, Dow Chemical Company.

"Service of Chemistry to Human Nutrition," by C. A. Elvehjem, University of Wisconsin.

"Service of Chemistry to Agriculture," by C. E. Friley, Iowa State College.

"Service of Chemistry to Industry," by Gustav Egloff, Universal Oil Products Company.

"Effect of New Resistant Materials on Modern Industrial Chemical Development," by James A. Lee, Chemical and Metallurgical Engineering.

"Effect of Economic Conservation of By-products on Modern Industrial Chemical Development," by L. W. Bass, Mellon Institute of Industrial Research.

"Methods Analysis Programs in a Chemical Industry," by J. R. Bailey, E. I. du Pont de Nemours and Company.

"Effects of Instruments for the Chemical Industries on Modern Industrial Chemical Development," by John J. Grebe, Director of Physical Laboratory, Dow Chemical Company.

Of particular interest to teachers of chemistry was the conference between leading representatives of industry, colleges, and universities, held Friday, December 13. The topic of this conference was "The Modern Chemistry Curriculum—Its Strength and Weakness." No papers were prepared, the discussion was informal, and the meeting was not open to the general public; it was also understood that no reporters would be present. Some of the topics brought up were:

1. Training in the written and spoken word needed by the chemist.
2. The personality factor in the work of the chemist.
3. Training in fundamentals versus specialization in the college curriculum.
4. The role of industry in training of specialized technics.
5. The training of the young chemist after hiring in ability to discuss and write reports, by: seminars, participation in learned societies, etc.
6. The difficulties in attempting to change acquired habits so late in life.
7. The desirable educational background of the young chemist aside from the training in chemistry and allied subjects.
8. The training of young chemists to understand and translate the data they obtain.
9. The value of the Master's degree.
10. Breadth of education versus more technical training.

Among those who participated in the discussion were: Carl Miner, who acted as chairman; N. F. Peters, Director of Research, Quaker Oats Company; Allan Abrams, Technical Director, Marathon Paper Company; E. C. Britton, Director of Organic Research, Dow Chemical Company; Gustav Egloff, Director of Research, Universal Oil Products Company; Per K. Frolich, Director of Chemical Laboratories, Standard Oil Development Company; L. W. Bass, Assistant Director, Mellon Institute; W. L. Evans, Ohio State University; A. H. White, University of Michigan; L. W. Wallace, Research Director, Crane and Company; Farrington Daniels, University of Wisconsin; H. Schlesinger, University of Chicago; Henry Gilman, Iowa State College; A. M. Patterson, Antioch College; K. H. Hoover, Commercial Solvents Corporation; V. Conquest, Director of Research, Armour and Company.

The management of the JOURNAL wishes to extend its thanks to the members of the Student Associates of the Chicago Section of the American Chemical Society for helping with its booth.

Vladimir Vasil'evich Markovnikov

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FEW Russian chemists of the last century have become well known outside the boundaries of their own country. The limited circulation of Russian scientific periodicals probably accounts for the failure to recognize the accomplishments of a group of men whose names should be as familiar to chemists as those of their leading contemporaries in Germany, France, and England. An important member of this group is V. V. Markovnikov, whose valuable contributions to the theory and practice of organic chemistry entitle him to a high place in the history of chemistry.

Vladimir Vasil'evich Markovnikov[1] was born December 22, 1838, in the village of Chernorech, near Nizhni-Novgorod. His father was a lieutenant in the Chasseurs Regiment stationed in the town. Shortly after the birth of his son, the father inherited a small estate at Ivanovsk, near Knyaginin, and, retiring from the army, went to live on this property. Here young Markovnikov spent most of his childhood.

His early education was in the hands of the village priest, and his principal reading was concerned with the lives of various saints and martyrs. Markovnikov quickly developed a passion for books, and read everything that fell into his hands. In addition to the Russian romances that were available, he discovered the works of Dickens and Thackeray, and even a three-volume work on tactics which his father owned, but had never read.

At the age of ten he entered the gymnasium, and in 1856, at the age of eighteen, he completed the course and enrolled in the Finance Division of the Juridical Faculty at the University of Kazan. The studies in this division concerned chiefly economics, political science, and law, but two years of chemistry were also required. In later life, Markovnikov said with regard to his rather unusual preparation for chemistry, "Not only have I never regretted that I completed the course in the Finance Division, but even now, with particular satisfaction, I consider myself an economist. In order to understand the phenomena of nature and control her laws, I have chemistry and physics and enough knowledge in the natural sciences. However, the Finance faculty gave me a basis for study and understanding of phenomena in the fields of economics and industry which the physical sciences would never have given me, and this I have often been able to use."

The chemistry given in the third year of the Finance Division included both lecture and laboratory in organic chemistry. Here Markovnikov came under the influence of the best Russian chemist of the period, A. M. Butlerov.[2]

Butlerov at this time (1858) had just returned from his first trip abroad and his study with Wurtz in Paris, and was at the beginning of his brilliant theoretical work on the development of the structural theory.

VLADIMIR VASIL'EVICH MARKOVNIKOV, 1838–1904

In many respects, Butlerov's views as developed during this and the next few years were the most advanced of those of any organic chemist of his time, and it was Markovnikov's good fortune to be in a position to watch this development, and even to add something of his own to the result.

Markovnikov's interest in chemistry steadily increased, and when he was allowed to assist Butlerov in preparing a lecture syllabus which involved the professor's theoretical ideas, his future course was decided. Although he took the degree of Candidate in the Finance Division in 1860, he was immediately afterwards chosen as Butlerov's assistant in the chemical laboratory.

The physical equipment for work was very poor, laboratory supplies and space were scanty, and funds for carrying on research were almost entirely lacking. The university supported the work as far as it could, but with an enrollment of not more than three hundred students, it was able to supply little help. In 1859, when a new bench was needed for the laboratory, Markovnikov collected twelve rubles from the chemistry students and to this Butlerov added ten rubles to complete the purchase. In 1863, however, a more generous allowance was made, and after that matters were not so difficult.

As Butlerov's assistant, Markovnikov was active in

[1] KABLUKOVA, "V. V. Markovnikov. A biographical sketch and short survey of his scientific work," *J. Russ. Phys.-Chem. Soc.*, **37**, 247–94 (1905).

[2] LEICESTER, "Alexander Mikhailovich Butlerov," J. CHEM. EDUC., **17**, 203–9 (1940).

research almost from the time he entered the laboratory. His first published paper, "A New Polymer of Aldehyde," appeared in 1860, and others followed at frequent intervals. In 1862 he was appointed lecturer in inorganic chemistry, and a year later analytical chemistry was added to his teaching duties.

During this period, Markovnikov was naturally absorbed in the theoretical teachings of Butlerov and in watching the development of the whole idea of the structure of organic compounds. He published a paper on "The History of Teachings on Chemical Structure" in 1865 and incorporated much of this material in his Master's thesis which he presented in the same year. This thesis, "The Isomerism of Organic Compounds," covered the historical side of the structural theory in considerable detail, discussed the contemporary state of the theory, and gave a critical estimate of the leading workers in the field. It is interesting to note that, although he recognized the part which Kekulé had played in the development of the structural theory, Markovnikov was rather critical of Kekulé's tendency to overemphasize the importance of his own work. As was probably natural in an ardent admirer of Butlerov, Markovnikov felt that Kekulé received too much credit. He summed the matter up in these words, "Reading Kekulé's papers, we get the impression that all the ideas published in recent years on the internal bonds of atoms in molecules had already been developed and published in Kekulé's testbook. Future students will decide for themselves whether Kekulés' position agrees with the present basic constitutional theory. They will not give all the credit to one man, as has been done in the case of the unitary theory, but will see that it was worked out gradually by the labors of many chemists, among whom Kekulé, in justice, will hold an honored place." Markovnikov concluded his dissertation with description of the preparation and properties of isobutyric acid. This was the first example of isomerism in the monocarboxylic acid series. The thesis was highly praised by Butlerov, and the Master's degree was awarded in 1865.

In the same year, Markovnikov married Lybova Rychkov, the daughter of a Kazan friend. At about the same time, he received a fellowship for two years of foreign study. This fellowship was planned to prepare Markovnikov for the professorship of technology when he returned to Kazan. However, Butlerov knew that his real interest lay in the field of pure rather than applied chemistry; when Myasnikov, who had been chosen for the chair of chemistry, suddenly died, Butlerov encouraged Markovnikov to work in pure chemistry. This the young man did, and though the terms of his fellowship were not altered, he devoted himself entirely to theoretical studies, with no objection from the Ministry of Public Enlightenment which had granted him the stipend.

In the summer of 1865, Markovnikov went to Heidelberg, where he worked with Erlenmeyer, completing the studies on isomerism which he had begun with Butlerov. He then visited Berlin and worked for a time with Baeyer, and at length went to Leipzig, where he spent the major part of his foreign visit in the laboratory of Kolbe.

In Leipzig, Markovnikov devoted much attention to analytical chemistry, a subject which was then very much neglected in Russia, but his experimental work continued to be in the field of organic chemistry. At first he worked on the reactions of acetoacetic acid and its relation to isobutyric acid, but he was soon attracted to studies of halogenation reactions, and then devoted all his efforts to the problem of the reciprocal effects of atoms in a molecule. The founders of the constitutional theory had studied chiefly the exact pattern of the atoms in a molecule, and had used chemical reactions as a tool to show what the positions of these atoms were. Markovnikov realized that the nature and position of these atoms could affect the reactions of the other atoms located nearby in the same molecule, and in this way affect the reactions of the molecule as a whole. In these ideas he was clearly the forerunner of the modern school of the application of the electron theory to organic chemistry, but at that time the concept was completely new, and Markovnikov pioneered in the field. It is possible to realize how completely foreign such ideas were to the minds of the chemists of that day when we read that Grebe once asked Markovnikov, "Why is the chlorine in acetyl chloride so greatly different from that in ethyl chloride?"

In his position at Leipzig, Markovnikov was somewhat set apart from the other students, who were working for degrees, and he worked chiefly on his own problems, with the guidance and advice of Kolbe. Kolbe was a curious mixture of advanced ideas and ultra-conservative opinions. He had developed a system of writing formulas which contained almost all the elements of the structural theory, but he fought bitterly against the Kekulé formulation. He refused to recognize the new theories of atomic weights, and persisted in using the old system in which oxygen had an atomic weight of eight. Naturally Markovnikov, fresh from Butlerov's laboratory, frequently disagreed with Kolbe, but the latter, even when bested in argument, would walk away, saying, "You will see that I am right. Many whom I long ago convinced did not wish to confess it, but now say the same thing. So it will be in this case."

Finally, when Markovnikov was ready to leave Leipzig and was preparing to publish his results, he had a conference with Kolbe. He tells the story as follows: "The dispute came down to the old story of oxygen. 'You don't understand me because you are not accustomed to my formulas,' said Kolbe. 'I will express your ideas in your own formulas.' 'Now,' I thought, 'Now, Herr Professor, you will break down.' He began to write, and stopped halfway through a formula, thought a moment, then laid down the pencil, saying, 'Yes, you are right.' Then he completed the formula and repeated, 'Yes, yes, that is right; how true,' and somewhat confusedly began to explain something.

I quickly withdrew, to spare the self-esteem of an honored master. A year later, I received from him a pamphlet on another of our disputed questions. In it he developed his theoretical ideas in detail, but he now wrote the weight of oxygen the new way."[3]

Although Markovnikov recognized the advantages of foreign travel and the value of the exchange of ideas with other scientists, he was strongly nationalistic at heart, and deeply regretted the backward state of science in Russia. Throughout his writings we constantly find references to the disregard of Russia by the rest of the world and to the neglect of Russian scientific work. In 1867 appeared a paper in which he set forth the beginning of his theories on the reciprocal reactions of atoms. After his death, a reprint of this paper was found on which he had written, in October, 1898, "In this paper is given a short summary of my views which were more accurately expressed in my doctoral dissertation. The laws deduced from this govern many important reactions, and were then perfectly new, and some even contradicted very authoritative opinions (Kekulé's). Naturally, my ideas as a young chemist, and a Russian at that, remained without influence, and though later they were confirmed and accepted by everyone, yet their first author was forgotten. Every one agrees, for example, that in acids the hydrogen nearest the carboxyl is first replaced in substitution reactions, but no one mentions that I first stated this law. To what degree this reciprocal influence of atoms is still not clear even to some eminent chemists is shown by the recent paper of V. Meyer on the order of substitution of hydrogen in polyhalogenated hydrocarbons. Schorlemmer in 1867 asserted that on chlorination of paraffins he obtained the chlorides of normal alcohols. I showed that his mixture contained chiefly secondary chlorides. This fact had not previously been explained. The truth of this reaction is now recognized, but no one has generalized the law, and I know of no handbook in which the statement is placed on any general basis. Such facts are usually stated as the result of empirical findings. In the course of my lectures, I always give the general principle, especially when, in the descriptive portions, confirmations of the general law appear."

Markovnikov returned to Kazan as docent in chemistry in 1867. He at once began work on his doctoral dissertation, for which he received the degree of Doctor of Chemistry from Kazan on April 30,1869. His thesis was entitled "The Reciprocal Effect of Atoms in Chemical Compounds." In the introduction he stated, "The structural theory is the external mechanism whose action directs and regulates the reciprocal effects of the atoms. This effect is the deeper reason which gives meaning to all the results of the mechanism." The experimental work involved a study of the replacement of hydrogen by bromine in various isomeric butyric and hydroxybutyric acids. From these experiments he drew a number of important conclusions as to the positions taken by the substituents with reference to the other atoms in the molecule. Thus, he showed that when a halogen has entered the molecule, further addition of halogen occurs on the same atom, and if oxygen is present, the hydrogen nearest the oxygen is replaced by halogen. He concluded with an elaborate demonstration of the principle still known to the organic chemist at Markovnikov's Rule, and showed how these ideas could be applied in determining the structure of organic compounds.

This thesis was an outstanding contribution to the contemporary theories, but unfortunately, Markovnikov allowed his nationalistic feelings to carry him away, and, although Butlerov, now a professor at the University of St. Petersburg, urged him to translate it, he refused to publish it in any language except Russian. In consequence, the ideas which he put forth remained unknown to most chemists, and were gradually expressed by others at a later date. Markovnikov himself afterwards said that he regretted that he had not followed Butlerov's advice. It was not until 1899 that Michael, in Germany, pointed out the contribution which Markovnikov had made. He wrote, "The idea of the reciprocal effect of atoms in a molecule was first pointed out by Markovnikov and by Baeyer. The latter applied his treatment only to a limited field, and therefore, the great service of Markovnikov is that he not only considered the question as a general one, but also gave a number of rules, important in the highest degree, which he deduced from his ideas."[4]

When Butlerov was called from Kazan to St. Petersburg in 1868, Markovnikov was appointed extraordinary professor of chemistry to take his place, and in 1870 he was raised to ordinary professor. In October, 1871, Markovnikov and six other Kazan professors resigned in a body, following political differences with the rector. Before the resignation could take effect, the University of Odessa offered him the chair of chemistry, which he accepted and assumed in December, 1871. The laboratory at Odessa was one of the newest in Russia, and was very well equipped. In the two years he remained there, Markovnikov published five papers. His work continued along much the same lines as before, and he developed his theoretical ideas still further.

Hardly had Markovnikov settled at Odessa when he was approached by the University of Moscow. This institution was noted for its historical-philological faculty, but it was very weak in sciences. The professor of chemistry had recently died, and the university wished to strengthen its faculty in this field, and so turned to Markovnikov in the summer of 1872. Markovnikov visited the University and found that there were almost no laboratory facilities. For six months he was undecided, but at last accepted the position, and in July, 1873, he took over the chair of chemistry.

[3] MARKOVNIKOV, "Recollections and traits from the life and activities of A. M. Butlerov," *J. Russ. Phys.-Chem. Soc.*, **19**, Butlerov Memorial Number, 69–96 (1887).

[4] MICHAEL, "Some laws and their use in organic chemistry," *J. prakt. Chem.*, **60**, 288 (1899).

Although he had prepared plans for a new laboratory before coming to Moscow, it was not until 1887 that these plans were finally carried out. The change to a new location involved much administrative and organizational work. The former professor of chemistry had died two years before, and no chemistry had been given until Markovnikov arrived. Therefore, he had to give chemistry for all the students in science, medicine, and pharmacy for those two years, as well as for the students of the current year. The attempts to organize the laboratory and catch up with the teaching naturally took much time, and for several years the output of research by Markovnikov and his students fell off. However, as more and more students were attracted by the skill and ability of the new professor, the number of papers published again rose to its former level.

Markovnikov always discussed his problems fully with the students around him, and encouraged them in their own plans and problems. He was especially careful to give full credit to his students for their own work, and never placed his name on a paper unless he had played an important part in its preparation.

In 1881 appeared Markovnikov's first paper on the study of the organic compounds in petroleum. This represented an important shift in the direction of his research, and with it he entered the second phase of his scientific career. The work was begun at the suggestion of an oil refiner who furnished funds for the study over a two-year period. Markovnikov was especially glad to take up this problem, since it appealed to his patriotic spirit, and he felt that he might be able to accomplish something of value for the Russian petroleum industry. Other Russian chemists did not share this view. Professor Alekseev of Kiev, in an annual review of the chemical literature, expressed regret that Markovnikov was deserting the field of pure science. This was not at all the case, however. His work in the new field of hydrocarbon chemistry and the constitution of the naphthenes was of great theoretical importance, as well as being a valuable contribution to the knowledge of petroleum and its products. Although the financial support of the industry was later withdrawn, Markovnikov had become so interested in the work that he continued in this field for the rest of his life.

The study involved the isolation of a very large number of individual compounds, and he was aided in this work by the laboratory assistant, Mikhailo, whom Decker[5] calls "an artist in fractional distillation." Mikhailo was illiterate, but he "managed, with the aid of an unbelievable memory, to work out the thousands of oil fractions whose place in the problem he recognized, sometimes after a whole year, by hieroglyphics which he alone understood."

Markovnikov at first thought the naphthenes which he obtained from petroleum consisted of ring compounds with varying ring structures, but he soon convinced himself that almost all of them were hydrogenated aromatic compounds. He synthesized many of them and developed new methods which were applicable to all organic chemistry. He also studied a number of terpenes and became interested in the problem of ring compounds which contained more than six carbon atoms. This work led to the preparation and study of cycloheptane. In addition, he carried out a number of studies with Konovalov on the nitration of paraffin and naphthene hydrocarbons which led to important results in aliphatic chemistry. Toward the end of his life, Markovnikov combined both the earlier and later phases of his researches in a series of excellent papers on the effect of atoms and groups on the reactivity of various hydrocarbons.

Although his chief activities were thus in the field of organic chemistry, Markovnikov had a wide variety of other interests. During the Russo-Turkish war he was in charge of much of the sanitation, and visited the battle front on several occasions in connection with the disinfection of hospitals and troop trains. During this work, he himself contracted typhus and was seriously ill for some time.

He inspected the salt lakes of southern Russia and began to develop plans for their industrial exploitation. This work was discontinued, however, when a large supply of rock salt was later discovered elsewhere.

He was much interested in promoting closer relations between chemistry and industry. At that time, the few Russian factories in existence did not appreciate the possibilities of research, but Markovnikov was tireless in pointing these out, and he placed many of his students in the laboratories which he induced the industries to establish.

The University of Moscow was the first Russian institution to admit women to the laboratory, and Markovnikov early had women among his research group. He did much to popularize chemistry among the general public. At the same time, he retained his interest in economic questions and often contributed articles on economics and political science to the appropriate journals.

In 1881 the Russian universities, which had previously been allowed a large measure of academic freedom, were placed under strict government supervision. A separate police force was established to watch them, and both students and professors were subject to a strict discipline. Markovnikov was far too strong a character to be satisfied under these conditions. In 1893 the storm which had long been brewing broke. An important official had been offended by a student at the university, and demanded that he be presented with an address of apology by the faculty. Markovnikov refused to sign this. Shortly afterward he was deprived of his position and official residence, with no reason given. Decker says, "For the almost sixty-year-old father of a numerous family, this was a heavy blow. I can still see the thickset, energetic figure of Markovnikov, with snow-white hair and beard framing the face, as with gleaming eyes and an expression in which pain and anger mingled he cried out, 'I have

[5] DECKER, "V. V. Markovnikov," *Ber.*, **38**, 4249–59 (1906).

depended most deeply on my teaching and research position, and now it seems that it will be taken from me.'" However, Markovnikov was still permitted to work in the university, of which he was made an honorary member, and some of his best work was done after this blow had fallen.

In 1901 Markovnikov celebrated the fortieth year of his scientific activity. Telegrams and letters of congratulation came to him from every important chemist and laboratory in the world. The American petroleum industry was especially grateful to him for his contributions in its field, and sent him many messages of congratulation. In a speech which he made during this jubilee, he said, "If I regret anything in my life, it is that I have not worked enough, and if I were called on to advise a younger comrade, I would say, work."

This advice he himself continued to follow vigorously, although after a time his health began to fail. In December, 1903, he visited St. Petersburg and presented a review of his work to the Russian Chemical Society. On his return from this trip he became ill, and on February 11, 1904, he died at the age of sixty-six.

An Apparatus for Photoelectric Titrations

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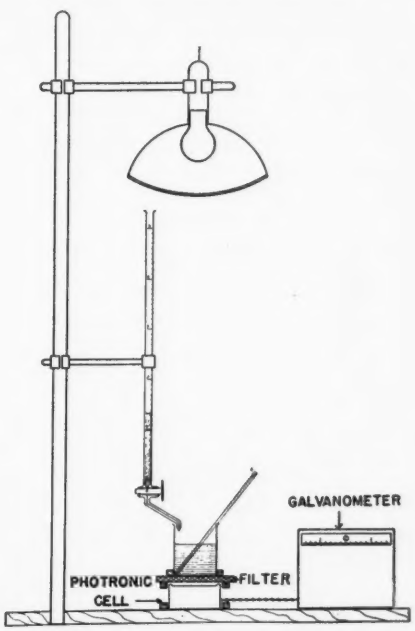
THE simplicity, sturdiness, low cost, and ease of cleaning and replacement of parts in the apparatus in the accompanying sketch are self-evident. It differs in principle from the usual photoelectric arrangement in that light is passed vertically, rather than horizontally, through the solution whose depth of color is to be measured. It may be used for titration to some given colored endpoint, or without the buret for comparing different intensities of the same color in different solutions. For example, for the particular use for which it was designed, it was fifty times more sensitive than the eye in detecting a color change in a pink phenolphthalein solution.

The specifications which follow serve to emphasize the merits of the apparatus. The galvanometer is a Leeds and Northrup portable reflecting galvanometer, D.C., No. 2420A, sensitivity of thirty millimeters deflection per microampere. Uniform illumination is achieved with an ordinary drug-store bed-lamp of the spotlight bull's-eye variety. A 50-ohm slide-wire resistance in series with a 60-watt bulb in the bed-lamp controls intensity of illumination; and the 3.5-volt lamp of the galvanometer is also lighted on the same current by tapping off an appropriate length of the resistance. A B-battery should be used if the 110-A.C. is not steady. The photosensitive cell is a Weston Photronic Cell, Model 594. Increased sensitivity is achieved by covering the cell with a filter which excludes light of the same color as the solution to be measured. For red solutions a 3″ × 3″ square of Corning Glass Light Filter G 984 B, 4 mm. thick, was used. The cell in which the colored solution is placed is an ordinary 50-ml. pyrex beaker. This size exactly fits the well of the Photronic Cell; and different pyrex beakers are sufficiently identical in their transmissions in the visible spectrum so that they may be used interchangeably, a factor of considerable advantage. When a filter is employed, automobile cork gaskets are glued onto both sides of the filter, as illustrated in the figure. To clean the photocell and filter, they are simply lifted from each other, and from the base board.



APPARATUS FOR PHOTOELECTRIC TITRATIONS

Reproducibility of the galvanometer is assured during titrations by checking frequently against two standard deflections namely, (1) with the light passing through the G 984 B filter and (2) with the light passing through both a square of Corning Glass "heat resisting yellow" Noviol O filter and the G 984 B filter.

Some Problems of Chemotherapy

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THE cures of many bacterial infections by sulfanilamide and several of its derivatives during recent years have overshadowed all other developments of chemotherapy. They demonstrated not only the curative effects of the new drugs but also the danger of unanticipated poisonous effects. Not since the discovery of arsphenamine and neoarsphenamine by Ehrlich, the founder of chemotherapy, over thirty years ago, has there been more interest in this branch of medicinal chemistry than now, and it seems appropriate to review a few of the experiences and underlying theories of this field.

A chemotherapeutic agent is a chemical which will kill or damage a parasite without injury to the host. The parasite may range in size and complexity from an intestinal tape worm of several meters length, to the smallest cocci which cause disease. The host to be cured may be man himself but, on the other hand, man's domesticated and farm animals are also susceptible to similar diseases which are often curable by similar drugs. In this article, only such drugs will be considered as are used in the treatment of infections caused by pathogenic microörganisms.

An ideal chemotherapeutic agent which would remove the cause of the infection without any undesirable side action has never been found, probably because both the host and the parasite are organisms containing a complex of proteins, enzymes, etc., and we can only hope to aim chemically at the protoplasm or the metabolism of the invader without hitting the host at the same time. But it is possible in some cases to devise compounds which will impair parasites when used in doses much smaller than the amount which will produce toxic effects in the host. If the curative dose is c, and the tolerated dose is t, we say the substance has a chemotherapeutic index of $c{:}t$. The smaller this fraction the better suited is the compound as a therapeutic. The chemotherapeutic index of a compound may vary in different animals or for different parasites in the same animal and even for different strains or stages of evolution of the same parasite.

Test tube experiments (experiments *in vitro*) rarely have any significance for the final clinical evaluation of the drug. Compounds which have either no action on a parasite *in vitro*, or act only extremely slowly in higher concentrations, may be powerful drugs *in vivo*, in the living host, or vice versa. But even a drug which has proved to be satisfactory in laboratory animals may be useless for the same infection in other animals or in man.

The pathogenic microörganisms which the chemotherapist has to deal with are representatives of the lowest forms of plant and animal life. Among the former are, *e. g.*, bacteria and fungi, while among the lowest forms in the animal kingdom we find trypanosomes, dysentery-producing microscopic amoebae, malaria parasites, and other protozoa. There is often no sharp distinction between the two groups; thus, the spirochetes which cause syphilis stand at the border line between trypanosomes and bacteria. Again, the individual protozoa and bacteria of similar types may vary widely in their development, passing through several stages which may offer different degrees of resistance to chemotherapeutics. The following discussions will serve to illustrate certain methods of testing chemotherapeutically active compounds, and to call attention to a few important infectious diseases and their chemotherapy.

In testing a new drug, the toxicity is determined first in small animals, usually rodents, in order to obtain a general idea of the usefulness of the substance. Next, the drug is applied to a culture of a given microorganism in human blood *in vitro*. The white blood corpuscles, the leucocytes, are phagocytes and therefore part of the defense mechanism of the body against toxic invaders. A parasite living in a host will respire and digest, and will excrete products which, in the case of pathogenic microörganisms, cause the symptoms of the disease. The leucocytes, and also the bacteriophages of the blood meet the invader; bacteria are enclosed in leucocytes, a sharp increase in white blood corpuscles occurs to furnish enough defenders against the infection, and fever sets in, altering the normal temperature environment of the virulent invader. Antibodies are produced which counteract bacterial or protozoan toxins, and if the body is strong enough, it may check the infection without outside help. But usually, it is an unequal battle between parasites and blood cells, and the defense mechanism of the body calls for quick assistance.

The physician may come to the aid in two ways. He may have ready some specific antiserum which counteracts the toxins of the invading parasite and reinforces the exhausted supplies of the host. The other way is to administer a drug. Since the cellular structure of leucocytes is not unlike that of monocellular parasites, some drugs may injure the wrong cell and affect the leucocytes first. The trial of a drug on bacteria in human blood *in vitro* clarifies this problem; if the drug is to have any chance of being therapeutically successful, it must have a greater parasiticidal than leucocyticidal power.

Very little is known about the mode of action of any drug on microörganisms. A substance may attack a parasite by impairing its respiration or metabolism, *i. e.*, by chemical removal of products necessary for the life of the parasite. This may be determined by animal experiments, for instance in the case

of bacteriostatic or bactericidal drugs. A solution of the compound is injected intravenously, and its bactericidal power is tested at intervals after the injection by drawing blood from the animal, or by killing the animal and investigating the infected organ under the microscope. If the drug acts directly on the parasite without being altered in the body, the increase in bactericidal power of the blood must be at its maximum immediately after injection. If there is a delayed rise in the bactericidal power of the blood, the drug must have undergone a chemical change before it became active.

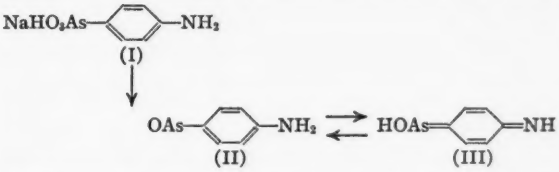
The alternative of direct chemical action of a drug upon a parasite is an increase of the defense mechanism of the host by the drug. The compound, or a derivative formed by chemical change in the body, may stimulate the cells which produce antibodies; or it may paralyze the parasite temporarily, inhibiting further multiplication and thereby giving the body time to resume its defense activity. These alternative actions may be tested by immunizing an animal with antiserum, and administering the drug after experimental infection. If the drug action is enhanced by previous immunization, the defense mechanism of the body must be involved in the parasiticidal action of the compound.

The first specific example of chemotherapeutic drugs to be presented is the group of aromatic arsenicals which act primarily on protozoan infections such as the spirochetosis of syphilis, the trypanosomiases of African sleeping sickness, and the amebiasis of amoebic dysentery. At a conservative estimate, six thousand arsenicals have been tested pharmacologically, but only five or six of these have been found of real clinical value. This is equivalent to stating that only five or six have been accepted widely by the medical profession. These drugs are arsphenamine, neoarsphenamine, mapharsen, tryparsamide, acetarsone, and carbarsone. They were all synthesized by Ehrlich before 1910, but four of them were introduced by others into therapy.

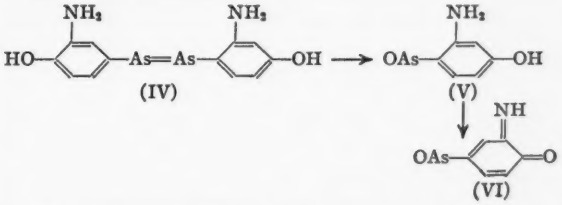
Arsphenamine and neoarsphenamine are standard drugs today for the treatment of the earlier stages of syphilitic infections. Their high molecular weight and their comparatively large particle size limit their effectiveness to those stages of the disease in which the spirochetes are still largely in the blood and in easily accessible organs, *i. e.*, in media which can be reached with water-soluble compounds, but in which they have not yet been enclosed in nervous or brain tissues behind less permeable membranes. The later stages of the disease, neurosyphilis and paresis, in which the spirochetes have been imbedded in lipid tissues, are treated with arsenicals of smaller molecular weight which may pass through the membranes of nerve cells.

One of Ehrlich's early compounds was atoxyl (I). It was abandoned on account of its very pronounced poisonous action on the optic nerve frequently leading to blindness. It is without much effect *in vitro*. The arsonic acid group is reduced to the arsenoxide group *in vivo*, probably by metabolic processes of the trypanosomes; it is likely that glutathione serves as a reducing agent. Atoxyl first kills the majority of the trypanosomes, then the spleen speeds up its antibody production and finishes the job. The participation of the body's defense mechanism can be demonstrated by removing the spleens of infected control animals. Much larger doses of atoxyl are needed for the recovery of these controls.

The tautomeric iminoquinone form (III) of *p*-arsinosoaniline (II), the reduction product of atoxyl, is regarded as the actively parasiticidal form of the drug:

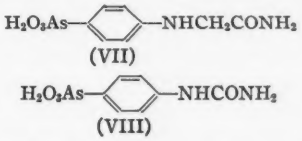


Arsphenamine (IV), on the other hand, is oxidized to 2-amino-4-arsinosophenol (V) and finally to an *o*-quinone imine (VI) in the liver; the latter compound carries out its mission.



When this mechanism of arsphenamine oxidation was recognized, the arsenious oxide derivative (V) was employed as an antisyphilitic in order to save the body the first step of the oxidation. It is used widely now under the name of mapharsen.

Tryparsamide (VII) was introduced into therapy by Jacobs and Heidelberger in 1919 and soon acquired prominence in the treatment of neurosyphilis and African sleeping sickness. It is much less toxic than atoxyl and can enter the spinal fluid to attack the spirochetes in tertiary syphilis, causing disappearance of clinical symptoms, but not always of serological reactions. Its diffusibility through nervous membranes had been thought to be mainly responsible for its activity in neurosyphilis, but other easily diffusible arsenicals of similar structure and molecular weight do not share this action. Tryparsamide cannot always be relied upon to act in advanced cases of paresis if irreparable necrosis of nervous tissue cells has occurred. The drug is successful only it the damage is repairable.



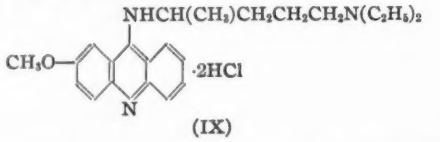
Carbarsone (phenylurea-*p*-arsonic acid) (VIII) is highly specific in the treatment of amoebic dysentery. It is able to cure cases in which other specific substances,

the alkaloid emetine, yatren (6-iodo-8-hydroxyquinoline-7-sulfonic acid), and acetarsone (stovarsol, 2-acetaminophenol-4-arsonic acid) have lost their effect. It had been known for thirty years and had been abandoned, as its use was not suspected until the investigations of Leake proved its specificity a few years ago. The large majority of aromatic and heterocyclic arsenicals have been tried out mostly for their action on spirochetal infections, but parasitologists and clinicians may well unearth new applications of some of the available compounds by systematic experiments with protozoan infections.

Malaria is perhaps the most important and widespread protozoan disease in man. It brings severe suffering to seventy or eighty million people, and death to at least one million every year. There are several hundred thousand malaria patients in the United States; the Canal Zone and our insular possessions are heavily infected. Vast areas of South America are practically unexplored because white men, at least, cannot withstand malaria in those regions. The native negro often develops immunity, after several generations have been exposed to the disease. His blood may contain enough Plasmodia to cause strong symptoms in non-immunized man, but the disease remains at a subclinical level in his body.

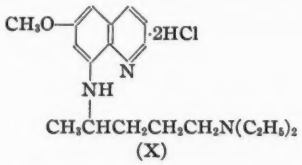
There are several types of malaria caused by closely related species of protozoa known as Plasmodia. Tertian malaria produces attacks every forty-eight hours; quartan every seventy-two hours, and subtertian every day, with almost constant fever.

The life cycle of the malaria Plasmodia takes place partly in the carrier, usually a female Anopheles mosquito, and partly in man. The infected mosquito introduces sporozoites which penetrate the red blood cells and develop into trophozoites in about twenty-four hours. The sporozoites are not attacked by any of the known antimalarial drugs. The half-moon shaped trophozoites round out and grow into schizonts after about fifty-two hours. These may be destroyed by both quinine and atebrin (IX) except in subtertian malaria, where they frequently are hidden in the endothelial cells of various organs; atebrin is much more effective in this case.



(IX)

If untreated, the schizonts undergo cell division and produce daughter cells, called merozoites, which are liberated into the blood stream. The merozoites are attacked by leucocytes, but these phagocytes cannot overcome the invader. The merozoites then invade young erythrocytes. Some of them develop into schizonts and repeat the cycle. Others become gametocytes, the sexual forms of Plasmodia. The gametocytes are affected by quinine or plasmochin (X) in tertian and quartan malaria, but in subtertian only by plasmochin. If a suitable mosquito sucks up gametocytes with the blood of an infected individual, the gametocytes develop further to gametes in its digestive tract.



(X)

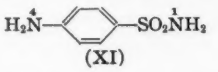
Fertilization takes place, growth through various stages of development, and after six days sporulation with formation of sporozoites. These break through to the salivary gland of the mosquito and may re-enter the cycle in a human host.

A few schizonts regularly escape annihilation by quinine and atebrin, and produce merozoites which lead to relapses of apparently "cured" cases. We do not know any drug which can be depended upon to eradicate all the stages of the malarial parasites, and research in this direction is needed immediately and urgently.

Quinine is the main alkaloid of the bark of cinchona trees which grow wild in equatorial South America. It has not been synthesized. Plantations in the East Indies yield the main world supply of the relatively large therapeutic doses which form our main protection against malaria. Quinine, atebrin, and plasmochin frequently produce toxic symptoms even when administered in ordinarily sub-toxic doses. Plasmochin may cause hemoglobinuria, atebrin nervous disorders, and patients treated with any of the three compounds will sometimes develop blackwater fever, although none of these compounds should be regarded as the prime cause of this condition. Thus, our available antimalarials do not approach the ideal definition of chemotherapeutic agents.

Several types of birds, especially canaries, serve as test animals for antimalarial compounds. Birds are not susceptible to the same Plasmodia as man but may be infected experimentally with related species. Compounds which cure avian malaria usually also show a favorable therapeutic index in man. But since the Plasmodia in birds and in man are not the same, and avian and human antibody production differs greatly, the trial of drugs in bird malaria must be confirmed always by a careful and extended series of clinical tests.

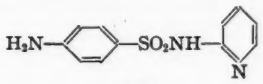
Bacterial infections withstood practically all attacks by specific drugs of a very high rate of dependability, until the work of Domagk (1934) on dyestuffs containing the aromatic sulfonamide group led to the subsequent introduction of *p*-aminobenzene sulfonamide (sulfanilamide) by the Tréfouëls in Paris in 1935.



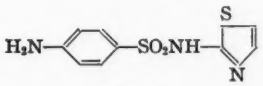
(XI)

In sulfanilamide (XI) we have a drug of high curative ability in a number of resistant bacterial infections, particularly hemolytic streptococcus and meningococcus

infections, gas gangrene, gonorrhea, and a number of others. The flood of work precipitated by the discovery of the chemotherapeutic properties of sulfanilamide has given us an enormous and ever-increasing number of compounds of related structure. Estimates place this number between 1500 and 3000, all prepared during the last five years. Of these, only a few have found their way into the clinics, notably sulfapyridine (XII), which is used extensively in the treatment of lobar pneumonia, and sulfathiazole (XIII), which has been applied successfully in pneumonia and staphylococcal septicemias.

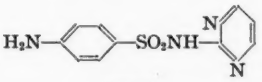


(XII)



(XIII)

Another N^1-heterocyclic sulfanilamide, namely 2-sulfanilamidopyrimidine (XIV) ("sulfadiazine"), was synthesized recently by Roblin and his co-workers.



(XIV)

It has shown great promise in preliminary studies. It is readily absorbed, which permits maintaining adequate concentrations of the drug in blood at lower dosage levels. Its sodium salt reacts less alkaline than that of related compounds, and there are indications that damage to the kidney might be less than for sulfapyridine and sulfathiazole.

In their chemical structure, these compounds follow a rule which has been established in sulfanilamide research. Substitution of the sulfonamide hydrogen atoms ($—SO_2NH_2$) increases the specificity of the compounds toward one type of bacteria. On the other hand, substitution of the aromatic amino group sharply decreases, and often abolishes bacteriostatic and bactericidal power.

Many authors believe that sulfanilamide is oxidized in the organism to phenylhydroxylamine-*p*-sulfonamide and that this derivative is the active bacteriostatic compound. This conclusion is supported by several observations. First of all, there is usually an initial bacterial growth period after administration of sulfanilamide, before bacteriostasis sets in. Direct administration of the hydroxylamine derivative is said to eliminate this lag; the compound also seems to show a more prolonged effect than sulfanilamide itself. The oxidation of sulfanilamide takes place in the blood or the tissues, since methemoglobin occurs during the therapy. Moreover, complete initial deprivation of oxygen (anaerobiosis) in blood and tissues prevents bacteriostasis, while an increase in the oxygen content of the blood enhances the action of sulfanilamide. There are indications that sulfanilamide prevents the oxidation enzyme catalase from supplying the bacteria with nascent oxygen; the cocci are killed by "suffocation."

Sulfanilamide derivatives do not attack equally well infections caused by the same parasite in different organs. Thus, sulfapyridine cures lobar pneumonia, but mastoiditis and brain abscesses caused by the same pneumococcus can scarcely be treated with this compound. Besides, not all strains of pneumococcus are affected equally by the drug. Some strains develop "sulfapyridine fastness" which interferes with the treatment of relapses. If, in the future, such drug-resistant strains of pneumococci should become more common, the usefulness of sulfapyridine may decrease. The only redeeming feature is that drug-fast strains are still susceptible to specific antisera.

One great bacterial infection which has withstood chemotherapy time and again is tuberculosis. A fairly large number of compounds, many of them containing iodine, iron, bismuth, copper, silver, and especially gold in organic linkage or in complex salt form, and also a few colloidal metals, will cure the symptoms of tuberculosis in isolated cases but never in a large number of pathologically similar cases. The tuberculosis bacilli are protected by a shell of wax which renders them resistant to the action of drugs. In this respect they resemble leprosy bacilli, but esters of chaulmoogric, hydnocarpic, and related fatty acids can get through the wax layer of these parasites. These esters are only partly successful in tuberculosis. Since waxes are soluble in facts, and vice versa, many bactericidal compounds have been esterified with fatty acids, or long alkyl chains have been attached to them, with the hope that their higher solubility in fats may help them to penetrate the wax coat, and that the "active" group of the molecule would then kill the bacillus. This has not had the desired effect. Some investigators have tried to cut the bacilli off from the surrounding tissues by treating the patients with silica preparations. The silica may enclose the bacilli, but the record of the success of this method is spotty.

We cannot yet answer the question whether chemotherapy will be an important factor in the treatment of virus diseases, or whether these infections will remain a domain of antisera. Several viruses have been recognized as complex nucleoproteins, and Stanley recently expressed the opinion that many more will be purified, and classified in the same way. We know a few cases in which drugs have helped to relieve symptoms caused by virus diseases, apparently by acting on the respective virus. Thus, sulfanilyl dimethyl sulfanilamide (Uleron) reduces the mortality of South African sheep in dropsy of the heart from 70 per cent to 5 per cent.

The author wishes to thank Dr. J. H. Sandground and Mr. H. A. Shonle, of the Lilly Research Laboratories, Indianapolis, Indiana, for many helpful suggestions in preparing the manuscript of this article.

"Let's Get Acquainted with Patent Law"

WILLIAM F. O'CONNOR, JR.
Manhattan College, New York City

EACH year witnesses a further expansion of the American chemical industry. Millions of dollars are being spent for new plants, new processes, and new products. Millions of dollars are being spent each year on the research which creates these new industries. But what is it that makes research successful? It is ideas, new ideas—new ideas that are guaranteed protection by the Constitution of the United States. This protection is in the form of a United States Letters Patent. Capital seeks security in investments and in the chemical industry that security is found in the protection afforded by a letters patent.

Our patent system is a living organization and as such it is constantly changing and growing. At the present time there are several rather drastic changes being considered for modifying the patent statutes. As chemists and as teachers of future chemists we should be interested in these changes which may vitally concern us in the future. Among such recommended changes are: (1) publication of allowed applications before they issue as patents; (2) establishment of a single Court of Patent Appeals; (3) provision for qualified scientific and technical advisers to the courts in equity suits involving patents; (4) reducing delays in examining applications; (5) a system of compulsory licensing of patents and the establishment of annual taxes. In the various scientific and trade journals, papers on patent law are appearing so frequently that one may well ask the question: "Why did we not hear more about patent law in school?" We may ask another question: "Why do we not include a few lectures on Patent Law in some of our courses that admit of a variation in content?" With United States patents being issued at the rate of some 800 per week, with 20 per cent of these chemical in nature, surely some effort should be made at least to touch upon the subject in one of the chemistry courses.

For the past four years at Manhattan College we have included, in the industrial chemistry course, not less than three full lectures on the fundamentals of the Law of Patents. This class meets twice weekly for one year.

It is the purpose of this paper to offer for your consideration and criticism the method we have found to be very successful (judging by the caliber of the work and by the enthusiasm of the student response). We cannot expect to teach the fine points or the specialized technic of the Patent Attorney who has had many years of diversified experience, but after several hours of guided preparation students should have at least a working knowledge of the subject. The sources of suitable material for inclusion in these lectures are briefly discussed, the method of presentation is outlined, and several assignments are suggested in which the student studies actual patents and then prepares his own application for a letters patent on an invention conceived by himself.

There are several excellent sources of information on patents and patent procedure which should be consulted. The pamphlet on "Patent Laws" (*1*) contains the Constitutional provision and the revised statutes under which our patent system operates. The "Classification Bulletin of the U. S. Patent Office" (*2*) gives the classification of subjects of invention and a brief glance at this booklet will immediately show the complexity and the diversity of the field of patents. "General Information Concerning Patents" (*3*) is of interest to the general public whereas "Rules of Practice of the U. S. Patent Office" (*4*) is of interest only to practicing attorneys. A very broad and non-technical background may be obtained from "Chemical Publications" (*5*) and "Library Guide for the Chemist" (*6*). The following texts should be available for reference: Deller (*7*), Perry (*8*), Rhodes (*9*), Rossman (*10*), Thomas (*11*), Wright (*12*). The journal articles (*13*, *14*, *15*, *16*, *17*, *18*, *19*) and those listed for supplementary reading treat of the various ramifications of the Law and its practice in considerably more detail.

THE SOURCE AND THE NATURE OF PATENT PROTECTION

In England in the sixteenth century when the royal funds were somewhat scarce, it became customary to grant monopolies in exchange for cash. The monopolies were usually granted on commodities and on everyday necessities. This procedure obviously led to many royal abuses, and in 1624 the Statute of Monopolies was passed, prohibiting the further granting of monopolies by the king except to "the true and first inventor of any manner of new manufacture within this realm."

In Article I, Section 8, of the Constitution of the United States we find: "The Congress shall have power . . . to promote the progress of science and useful arts, by securing for limited times to authors and inventors the exclusive right to their respective writings and discoveries." Note that the Constitution secures "the rights of inventors to their inventions," whereas in Great Britain a "privilege" is granted to inventors. In Great Britain and in other foreign countries the inventor must pay cash for this privilege. The United States is the only country wherein patents are not taxed. This fundamental difference is now the basis for one of the proposed revisions of the United States Patent Law.

The Court of Appeals for the Third Circuit (*20*) states: "An American Patent is a written contract between an inventor and the Government . . . The consideration given on the part of the inventor to the government is the disclosure of his invention in such plain and full terms that anyone skilled in the art to which it

appertains may practice it. The consideration on the part of the government given to the patentee for such disclosure is a monopoly for seventeen years of the invention to the extent of the claims allowed in the patent." The seventeen years starts on the date of issue, the day the Commissioner of Patents signs it.

One can readily see that the nature of the protection given to an inventor in a U. S. Patent is responsible for the large number of patents issued each year. Since the revised statutes of 1836 the Patent Office has issued some 2,150,000 patents, while to date French patents number 835,000, German 670,000, and British 500,000.

WHAT IS PATENTABLE?

"Patent Laws" (*21*) states "Any person who has invented or discovered any new and useful art, machine, manufacture, or composition of matter, or any new and useful improvements thereof, or who has invented or discovered and asexually reproduced any distinct and new variety of plant, other than a tuber-propagated plant, not known or used by others in this country, before his invention or discovery thereof, and not patented or described in any printed publication in this or any foreign country, before his invention or discovery thereof or more than two years prior to his application, and not in public use or on sale in this country for more than two years prior to his application, unless the same is proved to have been abandoned, may, upon payment of the fees required by law, and other due proceeding had, obtain a patent therefor."

In this regard the Court states (*22*) "The basic truth upon which rests a process may come to the discoverer suddenly and unexpectedly. He may not understand the law upon which the process operates, and he may be unable to explain the causes of certain phenomena, nevertheless if he be the first to give the world as a result of his method a new and valuable article of manufacture he is entitled to protection."

SECURING THE PATENT

After an invention has been conceived or made, application for a patent should be filed at the earliest possible date. It often happens that two or more persons may simultaneously but independently create the same invention and the establishment of priority is of utmost importance. Application for a U. S. Letters Patent is made in the form of a Petition to the Commissioner of Patents. These application forms may be obtained from any patent attorney or from any publisher of legal forms (*23*).

Special attention should be paid to the essential parts of a patent application, namely:

(1) Petition to Commissioner of Patents
(2) Power of Attorney
(3) Specification (word description of the invention)
(4) Claims (broad and narrow)
(5) Drawing (if required)
(6) Oath

Detailed discussions concerning the preparation of the application will be found in Rhodes (*24*) and Deller (*25*). Papers by Thomas (*15*) and Van Doran (*14*) should, by all means, be consulted.

It is hardly necessary to emphasize the importance of the specification and the claims, and their mutual dependency on each other. The necessity, the nature and the value of both broad and narrow claims in litigation, should be carefully considered. Here we have the heart and soul of the patent protection. Here we have the basis for infringement and for the litigation which, unfortunately, must follow. By definition, infringement is the unauthorized making, using, or selling for practical use, or for profit, of an invention covered by a valid claim of a patent during the life of the patent.

After the application has been filed, it is carefully studied by the patent examiner who indicates possible objections. When these objections have been removed, usually after several months, sometimes after many years, the patent is granted by the Commissioner of Patents.

When a patent is issued it is printed by the Government Printing Office, and any patent issued, provided the supply is not exhausted, may be obtained for the price of ten cents by writing to the United States Patent Office and asking for it by number.

THE PATENT REPORT ASSIGNMENT

After the fundamentals of the patent law have been discussed, the student obtains a particular patent and prepares a report on it. The patent chosen is thoroughly studied in its various phases and they are discussed at length in the report. This discussion includes an explanation of the patent, its relation to competitive processes, methods or products, its financial value, etc.; it is to be summarized by an intelligent, critical evaluation of the patent on such points as validity, utility, importance, etc. The steps to be followed are:

(1) Select the particular chemical product or process of interest to the student
(2) Obtain the Patent Number
(3) Have the selection approved by the instructor
(4) Procure the Patent by *number* from the U. S. Patent Office (send ten cents with order)
(5) Read collateral references in the field to which the patent applies
(6) Read collateral references on Patent Law
(7) Examine critically the salient features
(8) Prepare the report, including bibliography of all references consulted
(9) Submit the completed report accompanied by the copy of the Patent.

To date this has resulted in a collection of over one hundred patents that are used for study and debate by the class. Among these, of particular interest, may be found the following:

1,133,049	McKEE	Activated Carbon
942,699	BAEKLAND	Bakelite
2,029,387	PINE	Electroplating
1,875,760	SEVERAL	Electrolytic Magnesium
1,917,762	SEVERAL	Bromine from Sea Water
1,433,226	PORTER	Prestone
1,899,610	CLAPSDALE	Prestone
1,770,940	MEISSNER	Pure Aluminum
1,885,702	FINK	Tungsten Plating
1,581,188	FINK	Chromium Plating
2,038,988	BURGHART	Super-Pyro Anti-Freeze
1,722,174	BOOGE	Lithopone
1,968,793–7	.....	
1,993,431	.....	Drene Shampoo
2,046,242	.....	
1,586,175	BUCHANAN	Cyanogen Fumigant
968,832	CARROLL	Process for Aging Liquor
1,190,831	WERNER	Goiter Cure Necklace
1,392,767	KENDALL	Thyroid Extract
1,247,540	JONES	
1,247,542	JONES	Activated Sludge Process
1,282,587	JONES	
1,774,542	ARCHER	Aluminum-Beryllium Alloy
Plant Patent no. 1	VAN FLEET	Climbing Rose (Oct. 6, 1939)
Plant Pat. no. 207,	McKEE	
211–218, 225,	McKEE	Hybrid Poplar Trees
226, 228–230	McKEE	
1,608,661	NORDELL	Zeolite Water Softener
1,465,530	.....	Bath Salt Fat Remover

Another assignment is to have the student prepare a patent application for some hypothetical invention of his own, according to the following steps:

(1) Conceive a novel invention
(2) Work out the necessary details
(3) Obtain instructor's approval of the rough draft
(4) Obtain a printed application form from instructor
(5) Prepare complete application (being both inventor and attorney) as if for submission to the Commissioner of Patents

Particular attention will be paid to:

(1) Novelty of the invention
(2) Need for the invention
(3) Accuracy of the specification
(4) Adequacy of the claims

Thus we see the student has acquired a fairly complete background of the elements of Patent Law, has had first-hand contact with actual patents, and has had an opportunity to study the specifications and the claims that have been allowed in practice. The preparation of this report makes him realize the importance industry attaches to patents and the enormous amount of capital which may be invested because of a particularly far-reaching basic patent. In the final assignment the student makes use of the facts he has learned when he creates an invention of his own and protects this invention by drawing up the complete application for a United States Letters Patent.

It is hoped that these few remarks will arouse an interest in Patent Law, an interest that will give this most important but somewhat neglected topic a place both in our classwork and in our everyday lives.

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The Polarographic Method of Analysis

I. General Review of Electro-Analytical Methods

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FOR the past fifteen years, Professor Jaroslav Heyrovský[1] of the Charles' University, Prague, and his co-workers have been engaged in the development of a new electro-analytical method, the polarographic method. Today the essential principles of this method are well understood, and many laboratories all over the world are working out detailed applications which are beginning to be very useful in industry. It seemed worth while, therefore, to present a simple account of polarography in a form which can be used by teachers and students in courses of physical chemistry as well as in advanced courses of analytical chemistry. In this first article I shall discuss fundamentals of electro-analyses to bring out the fact that Professor Heyrovský has developed a method which is distinct from others in its principles. In subsequent articles I shall give directions for some typical polarographic analyses to be carried out with equipment so simple that it will undoubtedly be available in all student laboratories of physical chemistry.

The polarographic method resulted from studies of electrolyses with a dropping mercury cathode which were started by Heyrovský in 1922. After much laborious work in which all current–voltage curves were plotted by hand, Heyrovský and Shikata[2] developed an instrument which recorded these curves automatically; this they called a polarograph, and the records obtained with it, polarograms. With a large number of experimental data thus more easily available, the fundamentals of the new polarographic method became better understood and practical applications were worked out.

For a long time only those processes were studied in which the dropping mercury electrode was the cathode. Eventually, however, anodic processes and electrolyses with other small metallic electrodes were also investigated. Of the latter, at first only those were used which had a renewable surface similar to that of the growing drop of mercury; for instance, electrodes with scraped surfaces, or wire electrodes which were pulled through the solutions in such a way that only a small area was exposed at any one time. Finally, in recent years, even stationary or rotating electrodes with small surfaces were tested. It was found that current–voltage curves obtained with them could also be used for analytical purposes, after the information gained with the dropping mercury electrode was available. Thus by a circuitous route we have returned to the experiments of Nernst, who first suggested the use of a small electrode in combination with a large non-polarizable one for the study of processes at one electrode only. Today, however, we know considerably more about the phenomena occurring at such electrodes and can use them for analytical purposes.

The polarographic method may be defined as a method of analysis based on the electrolysis of a minute fraction of a solution in a cell consisting of one small, easily polarizable, and one large non-polarizable electrode. The voltage necessary for the electrolysis indicates the nature of the reacting substance, while the current observed is a function of its concentration. In this general definition, the dropping mercury electrode is only a special case, although undoubtedly the one of greatest practical importance at present. This sort of analysis is fundamentally new, as will become clear by a comparison with other existing electrochemical methods. These have often been described in textbooks but their fundamental principles have rarely been compared directly.

Electrochemical methods of analysis are based on two fundamentally different properties of particles dissolved or dispersed in solution; namely, the movement of charged particles in an electric field, and the ability of ions, atoms, and molecules to accept or give off electrons. The polarographic, as well as the electrolytic and potentiometric methods, make use of the latter property, while the conductometric and the two kinds of electrophoretic methods depend on the former. The last three methods are not, therefore, very closely related to the polarographic method; they are nevertheless included in this discussion because of similarities in their application.

METHODS DEPENDING ON THE MOVEMENT OF PARTICLES IN AN ELECTRIC FIELD

The Conductometric Method.—In an electrolyte, the current is carried by the positive and negative ions present. Electrical conductivity, therefore, indicates the ability of charged particles to move in an electric field under a given set of conditions. In order to measure this property accurately, one must be careful not to alter the system in any way by the procedure; for instance, the net movement of the particles must be zero, none of the components of the solution may be plated out on the electrodes, and the electrodes must not be polarized in any other way. With proper precautions, these requirements are fairly well met by the use of alternating current and relatively large electrodes of platinized platinum.

The practical application of the conductometric

[1] See J. CHEM. EDUC. **17**, 101 (1940).
[2] *Rec. trav. chim.*, **44**, 496 (1925).

method is based on two facts; namely, that a few ions have exceptionally high mobilities, and that many acids and some salts are either weakly dissociated or relatively insoluble. Making use of these conditions one can titrate the solutions and find an endpoint where the conductivity of the titrated solution changes abruptly. For instance, in titrating a strong acid with a strong base, one finds that the conductivity decreases linearly with the amount of hydroxide added, because the salt formed has less conductivity than the acid.

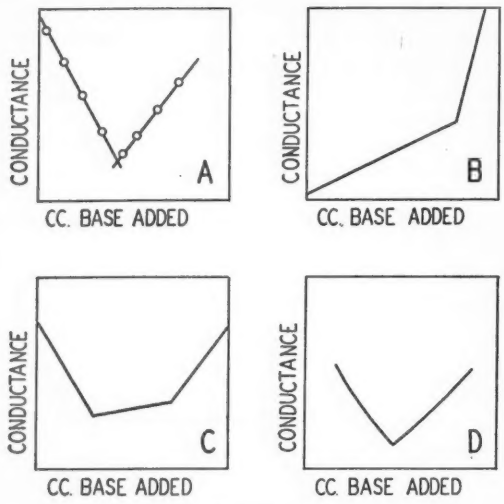

FIGURE 1

(*A*) Strong acid titrated with strong base
(*B*) Very weak acid titrated with strong base
(*C*) Mixture of strong and weak acids titrated with strong base
(*D*) Magnesium sulfate titrated with barium hydroxide

After the endpoint is passed, the conductivity increases again because of the increase in concentration of free hydroxyl ions. The exact endpoint is found by the intersection of the straight lines formed by plotting conductivity against the volume of solution added from the buret (Figure 1 (*A*)). Another illustration of the conductometric method is the titration of very weak acids with a strong base. Here the conductivity curve starts close to zero, rises slowly to the neutralization point, then rises rapidly because of free hydroxyl ions (Figure 1 (*B*)). A similar curve is obtained when the salt of a weak acid is titrated with a strong acid; for example, sodium acetate with hydrochloric acid. Up to the endpoint, the conductivity changes only by the difference between the conductivities of the chloide and acetate ions; but, when the endpoint is passed, there is a rise due to the excess of free hydrogen ions. In the titration of a weak acid with a weak base, *e. g.*, acetic acid with ammonia, the conductivity becomes constant, since the ammonia, present in excess, has very little conductivity. Even a mixture of strong and weak acids can be titrated with a strong base, and curves with two endpoints are obtained (Figure 1 (*C*)).

Finally, a precipitation reaction should be mentioned, such as the titration of magnesium sulfate with barium hydroxide (Figure 1(*E*)). In these reactions also a sharp endpoint is obtained, although the conductivity curves are not linear. However, unless its validity is proved, the endpoint cannot be trusted because the end-products often precipitate very slowly, adsorb material on their surfaces, or form unwanted complexes.

A special case of these conductometric measurements is the determination of the concentration of a dissolved substance by a single measurement of conductivity. This is possible only when the solution contains a single known electrolyte and when the conductivity of such a solution at all concentrations is known. If concentration is plotted against conductivity the unknown concentration can be interpolated.

Electrophoretic Methods.—In recent years these have come into prominence for analytical purposes upon realization of their value for the study of proteins and other colloidal material. In these methods the electrodes must be capable of carrying a large current, since direct current is passed through the cell to produce an actual movement of particles.

When the particles are large enough to be seen individually under the microscope, measurement of their movement by direct observation is possible. Unfortunately, most of the substances which are of interest have such small molecular or particle size that they are beyond the resolving power of any microscope. However, as has recently been shown, there are further possibilities for this technic, since particles of glass, quartz, collodion, and mineral oil, when coated with a film of protein, will move in the electric field in a manner which is characteristic of the protein and not of the particle.

The more general way of measuring the electrophoretic migration is based on the movement of a layer of the solution of the substance in the electrophoresis cell. This can be done in two different ways. In the *transference method* a known amount of electricity is sent through the cell, and the decrease or increase in the amount of substance in relation to a fixed level in the cell is determined by chemical or biological analysis. In the *moving boundary method* one measures the distance traveled by the boundary between the colloidal solution and a supernatant medium. The transference method has been used particularly for studying enzymes. Aside from its analytical value, it is of great importance for the separation of protein fractions and their preparation in a pure form. The moving boundary method is especially convenient for colored materials. Analyses of colorless substances are often possible by the use of ultra-violet light. However, a method depending upon refractive index, introduced by Tiselius, has outdistanced all others. If light is passed through the electrophoresis cell, it will be refracted at the boundary because of the refractive index gradient. This fact makes it possible to photograph the boundaries and observe their movement. Special

cells have been constructed to permit the establishment of very sharp boundaries between the protein solutions and the supernatant buffer solutions. The electrically charged components of the protein solutions then move across this boundary in the electric field with different velocities depending on their charge and size, and a number of different refractive index gradients result. This is photographed as a number of more or less diffuse lines resembling spectral lines. These so-called "electrophoretic patterns" can then be used for analytical purposes. Ingenious devices which cannot be described here have been constructed, with which automatic records of the movement of the charged particles can be obtained. These records have already been of great value in the field of biochemistry because they indicate different constituents of sera and extracts and their relative concentrations. Obviously, these methods require elaborate apparatus and expert manipulation. Their practical application, therefore, is still limited, and their use in physical chemical courses is at present out of the question.

METHODS DEPENDING ON OXIDATION AND REDUCTION

Of greater importance from a practical standpoint are the electro-analytical methods which are based on the ability of molecules, atoms, and ions to accept or furnish electrons or, in other words, their ability to become reduced or oxidized. The potentiometric method uses the potential established at special electrodes as an indicator of the composition of the solution and of the endpoint of a titration. The electrolytic method uses the current at a known voltage for the separation of the desired component from the solution for subsequent analysis. The polarographic method, while combining some of their features, differs from both these methods. Instead of removing one constituent of the solution completely by electrolysis, only a minute fraction of the solution in the neighborhood of a small electrode is electrolyzed, so that the body of the solution remains essentially unaltered. The potential established at the small electrode usually indicates the composition of only that small part of the solution which is in immediate contact with the electrode. It is seldom constant, because whenever current flows this composition changes. Therefore, the potential obtained polarographically and that obtained by the potentiometric method are identical only in exceptional cases. These statements will become clearer when some of the fundamentals common to all these methods are discussed.

When electrons are removed from an ion, atom, or molecule, the substance is oxidized; when electrons are added to a substance, it is reduced. Since free electrons cannot exist in solution, every electrochemical change involves a simultaneous oxidation and reduction. For example, ferrous ion is oxidized to ferric ion with the loss of one electron:

$$Fe^{++} \rightleftarrows Fe^{+++} + \epsilon$$

This reaction can only go to the right if some other substance is present which can take up the electron by being reduced, as, for example, stannic ion:

$$Sn^{++++} + 2\epsilon \rightleftarrows Sn^{++}$$

If ferrous ions and stannic ions are both present in solution, the electron transfer is direct from ion to ion, with the result that ferric and stannous ions are formed until an equilibrium is reached. This equilibrium will depend on the relative concentrations and on the relative capacity of the two reactants to hold electrons. If one substance is able to oxidize another and be reduced in that process, a definite difference in their ability to hold electrons (potential difference) is demonstrated. This difference can be measured and the various substances can be grouped into a graded series, the electromotive series.

To observe the magnitude of this difference, we must keep the ferrous and stannic ions apart by placing them in a cell with two compartments separated by a porous diaphragm. This will prevent their mixing; thus a direct transfer of electrons cannot occur. If we then place two electrodes into these two half-cells and connect them by means of a wire, we have completed an electric circuit which will bring about the same equilibrium conditions in the two solutions as if we had mixed them. However, it is now possible to measure the flow of electrons (the electric current) and the gradient in which these electrons flow (the potential difference). This can be done by means of an ammeter and voltmeter if the cell has a large capacity and the electrodes are not easily polarized; otherwise a sensitive galvanometer and potentiometer, which will minimize the flow of current, become necessary. Each half-cell consists of an oxidation–reduction system, made up of a reductant (having the greater number of electrons) and an oxidant (having the smaller number of electrons), and a suitable electrode. In the stannous–stannic system, the stannous ions are the reductant and the stannic ions the oxidant. In the ferrous–ferric system, the ferrous ions are the reductant and the ferric ions the oxidant. However, if an ion is reduced to the metallic state as, for instance, in the reaction:

$$Fe^{++} + 2\epsilon \rightleftarrows Fe$$

we have an oxidation–reduction system in which the ferrous ions are the oxidant and metallic iron is the reductant.

In the electromotive series, the normal hydrogen electrode has been chosen as an arbitrary standard with a potential of zero. All other oxidation–reduction systems are referred to it. There has been some confusion about the sign of the potentials. Clear definitions are given in textbooks on the subject; a study of these makes it obvious that a potential may be either positive or negative, depending on the way the electrode reaction is considered. In this discussion, the potential of the alkali metals in solutions of their ions will be considered negative, while the potential of the oxygen and chlorine gas electrodes will be considered positive to the hydrogen electrode.

The potential difference between two half-cells can be measured by applying to the electrodes a known opposing electromotive force (E.M.F.) from some outside source in such a way that no current flows in either direction. The known applied E.M.F. must then be equal to that existing between the two half-cells. If the potential of one of the half-cells is known, that of the other can then be calculated. It has been found that for each half-cell the potential at 30°C. is given by the following equation:

$$E = E_0 - 0.060/n \log a_{Red}/a_{Ox}$$

where n is the number of electrons involved in the reaction and a_{Red} and a_{Ox} are the activities of the reductant and the oxidant, respectively. For convenience we shall use the following less accurate form of this equation:

$$E = E_0 - 0.060/n \log [Red]/[Ox] \qquad (1)$$

where the brackets indicate concentrations instead of activities. If the ratio of $[Red]/[Ox]$ is unity, the last term in this equation drops out and we obtain E_0, the normal potential of the system. A graph of this equation for a one- and a two-electron change ($n = 1$ and $n = 2$) is given in Figure 2. It may be seen that, in the absence of one of the components of the system, the potentials become meaningless because they go off to infinity. The potentials are best defined in the middle of the curve where the ratio of $[Red]/[Ox]$ is near unity.

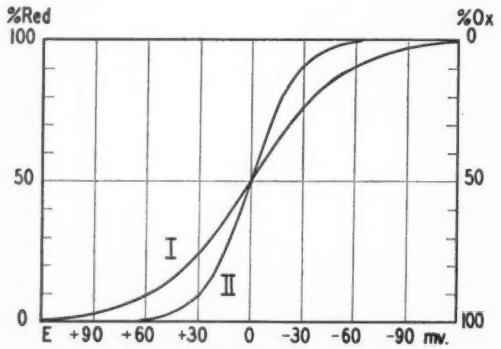

FIGURE 2

Relation between the potential, E, and the percentage reduction of a reversible oxidation–reduction system involving (I) a one-electron change, (II) a two-electron change

The electrodes used in these measurements fall into two classes. The *indicator* or indifferent electrodes are passive in the electrode reaction and merely indicate the potential of a system of which both oxidant and reductant are in solution. Noble metals serve for this purpose, or any other metal whose ions are present in such infinitely small concentration in the electrolyte that they cannot influence the ratio of the observed reductants and oxidants. In the other class of what I shall call *active* electrodes in this discussion, the electrode itself is one of the reactants of the oxidation–reduction system as, for instance, the less noble metals, the amalgams, or the gas electrodes. For use in equation (1), an activity or concentration value of unity is arbitrarily assigned to such an electrode if it is of a pure metal or if the gas is at atmospheric pressure. In the case of some amalgams, the concentration of the active metal in the amalgam is used.

The Potentiometric Method.—Depending on the type of electrode used we have two kinds of application of this method. The *active* electrode is specific with respect to one ion only and its potential is a function of the concentration of that ion. An indicator electrode can be used for many different systems provided their potentials fall within a range for which the electrode is suitable. In this case, however, the potentials are never a function of the *concentration* of the components of the system but merely a function of the *ratio* of oxidant to reductant. This difference though fundamental does not become very apparent in practice because, with the exception of pH measurements, almost all other determinations are made by titrations in which a marked change in potential at the endpoint is observed with both types of electrode. The titration curves do differ in one respect, however, which will be discussed later.

In measurements of potential, the flow of current is avoided as much as possible so that the conditions around the electrodes will not be changed. Sensitive galvanometers or electrometers or devices using vacuum tubes have been employed as null-point instruments. Modifications of the method in which use is made of bimetallic electrodes, differential titrations, and irreversible systems will not be discussed here because they bear no relation to the polarographic method.

The most widely known application of the *active* electrodes is the determination of hydrogen ions by means of the hydrogen electrode, the glass electrode, the quinhydrone electrode, or the antimony electrode. Under suitable conditions, every one of these acquires a potential which is a function of the concentration of free hydrogen ions. Special potentiometers have been designed in combination with the glass electrode and have been calibrated in such a way that the pH of the solution can be read instead of the electrode potential.

The only other application of this sort of measurement with *active* electrodes is the determination of the solubility of some difficultly soluble salts as, *e. g.*, silver chloride. The potential of a silver electrode in a saturated solution of this salt will give the concentration of the silver ions in equilibrium with it.

Of real practical interest are the potentiometric or electrometric titrations for which both types of electrode are used. Because of their close relation to polarographic curves, these titration curves will be discussed in more detail in the light of some examples.

Acid-Base Titrations.—We saw that the potential of the hydrogen electrode will give us directly the concentration of *free* hydrogen ions in a solution. This will

also be the concentration of the acid only if the acid is completely dissociated; otherwise a titration is necessary for its determination. For observing the point of neutralization or the endpoint in a titration, an indicator is usually employed which changes color at that point. The electrode potential can similarly be used because its change is maximal at the endpoint. In Figure 3 (*A*) we have an example of such a titration. Here the potentials are plotted against the volume of titrating agent (NaOH) added from a buret. In case the acid is dibasic there are two endpoints for the neutralization of each hydrogen ion. Two sharp breaks in the curve are observed if the two dissociation constants are far enough apart (Figure 3 (*B*), curve I). As they come closer together, the breaks become less distinct (Figure 3 (*B*), curve II). Often the endpoints in this case may still be determined with sufficient accuracy if the change in potential per unit volume of titrating agent is plotted against the volume of the titrating agent. The endpoints then appear as sharp peaks on the curve. Just as it is possible to titrate the two hydrogen ions of a dibasic acid, so it is possible to titrate a mixture of two different acids if their dissociation constants are sufficiently different. Here, however, their relative concentrations are also of importance; one acid should not be too much in excess of the other. Curves demonstrating titrations in which the limiting conditions are almost reached are shown in Figure 3 (*C*).

Precipitation Reactions.—Other active electrodes are used to indicate the endpoint in the case of precipitations. For example, in the titration of silver ions by means of chloride, the potential of a silver electrode changes rapidly as the last traces of silver are precipitated; a titration curve shows a sharp break at that point. Vice versa, a chloride solution can be titrated with silver nitrate; as long as chloride ions are still present to precipitate the silver ions the potential of a silver electrode stays relatively constant, but as soon as an excess of silver ions is added, the potential will change markedly. The curves resemble the one shown in Figure 3 (*A*).

Oxidation-Reduction Titrations.—In this case potentials are obtained with indicator electrodes, and here too a marked change of potential at the equivalence point is observed. The curves could be identical with the acid-base titration curves, except for the beginning. The corresponding theoretical curves for reductive titrations are drawn with an interrupted line into the graphs of Figure 3. The difference in the beginning of the curves is due to the fact that in the oxidation-reduction titrations one starts with pure oxidant or pure reductant. In either case the potential is theoretically infinity and, therefore, meaningless. However, in the acid-base titration shown above, we started with a finite concentration of hydrogen ions in equilibrium with the hydrogen electrode so that the potential is well defined and significant.

The middle of the curves are identical in both cases as may be seen by comparison of the framed section

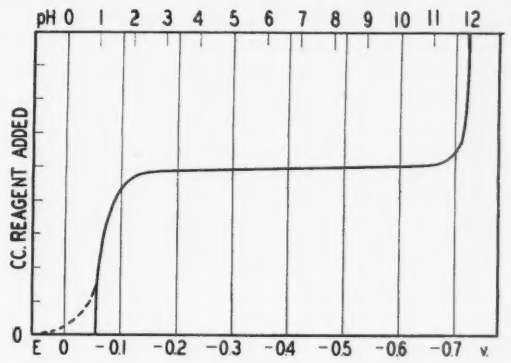

FIGURE 3A

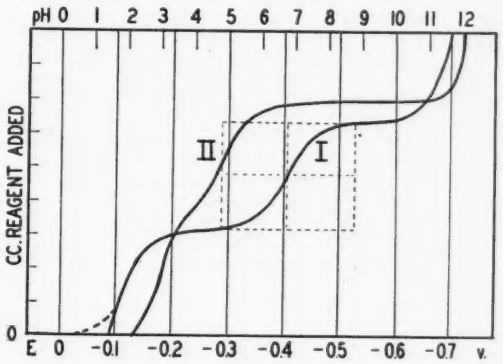

FIGURE 3B

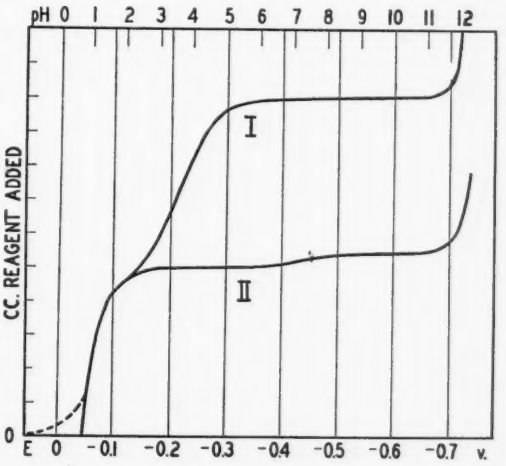

FIGURE 3C

FIGURE 3.—POTENTIOMETRIC TITRATIONS OF ACIDS WITH SODIUM HYDROXIDE

(*A*) Hydrochloric acid
(*B*) Curve I: Phosphoric acid
Curve II: Phthalic acid
(*C*) Curve I: 5 millimols of hydrochloric acid plus 5 millimols of lactic acid
Curve II: 5 millimols of hydrochloric acid plus 0.5 millimol of *o*-nitrophenol

of Figure 3 (*B*) with Figure 2. The reason for this is that in the titration of a weak acid with a strong base the concentration of free hydrogen ions and therefore the potential of a hydrogen electrode is a logarithmic function of the ratio of salt formed to the remaining acid, just as in the titration of an oxidant with a reducing agent the electrode potential is a logarithmic function of the ratio of reductant formed to the remaining oxidant. A formulation makes this point much clearer. The concentration of hydrogen ions in a solution containing a weak acid is given by the well-known equation:

$$[H^+] = k[HA]/[A^-]$$

which needs no further explanation. Substitute from this into the fundamental electrode equation (1), remembering that $[Ox] = [H^+]$, and that $[Red] = 1$ because the hydrogen is at atmospheric pressure. Then:

$$E = E_0 - 0.060 \log \frac{[1][A^-]}{k[HA]} = E_0 - k' - 0.060 \log \frac{[A^-]}{[HA]} \quad (2)$$

Now let the amount of strong base added to the weak acid be x. This will form an equivalent amount of salt which is completely dissociated so that $[A^-] = x$. The remaining, undissociated acid, [HA], will be $(1 - x)$. The ratio $[A^-]/[HA]$ in equation (2) will therefore be $(x)/(1 - x)$. Similarly let the amount of reducing agent added to the pure oxidant of an oxidation–reduction system be x. This will form an equivalent amount of reductant so that $[Red] = x$. The remaining oxidant, $[Ox]$, will be $(1 - x)$. The ratio $[Red]/[Ox]$ in equation (1) will therefore also be $(x)/(1 - x)$.

The end of the titration curves is similar in acid-base and oxidation-reduction titrations because the titrating agent used will always be in excess at the end of the titration and exert its influence on the potential.

The best known oxidizing agents in these titrations are permanganate, dichromate, ceric, iodate, and bromide ions, while the more important reducing agents are ferrous, titanous, chromous, and stannous ions. Analogous to the case of the acids, the oxidation-reduction titration curves will show a break for each change in valency of an ion or for each of several oxidation–reduction systems which are titrated simultaneously. For instance, the reduction of cupric ions to cuprous ions and their further reduction to the metallic state would give rise to a curve of the type shown in Figure 3 (*B*). Such curves are also produced at a suitable pH by some organic substances that form intermediate radicals (semiquinones) in a two-step oxidation or reduction. If the oxidation-reduction potentials of two systems differ sufficiently and their concentrations are in a suitable ratio, good separation of the two portions of the titration curve is obtained. With less favorable concentration ratios or with a smaller difference in the potential of the two systems, partial or complete overlapping of the two breaks will result. Again, Figure 3 (*C*) can be used as an example in which the limiting conditions are almost reached.

Before leaving this topic, we may point out that all these curves represent electrode potentials which reflect conditions in the *body* of the solution. Although almost identical curves will be obtained with the polarographic method, they will indicate only conditions at the electrode surface and not those in the body of the solutions.

While equilibrium conditions are assumed to exist in the above titrations, in practice marked changes in potential at the equivalence point are also often obtained in reactions where the potentials are definitely not reproducible and demonstrate an irreversible process. Such titrations serve their purpose but they are only empirical, and their validity must be proved in each case before they can be trusted.

The Electrolytic Method.—This method is concerned with the electrolytic removal of one of the components of the solution for further analysis. In practice it is confined to the deposition of metals or their oxides on the cathode and to the deposition of superoxides and insoluble salts on the anode. The cathode may be defined as that electrode at which electrons leave to enter the solution; the anode is the electrode at which the reverse process takes place. Platinum and mercury are most frequently used as electrode material. Sufficient voltage is applied to the cell to deposit the desired substance; when the electrolysis has proceeded until the solution contains less than a detectable amount of the corresponding metallic ions, the electrode with the deposit is removed from the cell, washed, dried, and weighed. The increase in weight is then due to the deposit. Care must be taken that only one kind of deposit is obtained and that part of it is not lost by side reactions with other components of the solution.

Theoretically, it should be possible to separate all the metals listed in the electromotive series whose potentials are different. Actually, the potentials must be rather far apart, in order to effect a separation, and to deposit only the more positive metal at an intermediate applied voltage. Sometimes it is possible to cause a wider potential difference by forming suitable complexes with the metal ions. When the deposition of the metal is complete, the current will practically cease flowing. However, as the concentration of the metal ions diminishes, fewer ions will reach the electrode surface in unit time and so it takes a long time to deposit the last traces of metal. This procedure, therefore, is of little value in practice, where speed is an essential requirement for a satisfactory analysis.

Numerous ways have been found to overcome these difficulties. Electrodes of special design and structure were built to present as large a surface as possible in a small volume of solution. These electrodes were rotated at high speed to insure contact with the last traces of metallic ions to be deposited. Also optimum conditions in the temperature of the bath were determined. Special, so-called addition reagents were added to the electrolytes in order to obtain smooth, firmly adhering deposits, free from admixtures. Finally, instead of applying just enough voltage to deposit the desired metal, analysts used larger voltages and regulated the

current instead of the voltage. Naturally, much larger currents were thus used and the fraction of the current effective in the deposition of the desired material, the current efficiency, was small, decreasing to zero toward the end of the reaction. However, in this fashion, analyses could be completed within a few minutes. By this method the separation of metals is carried out in groups and further separation must be made chemically. The electrolyte from which the metal is deposited must be such that the useless fraction of the current produces gases which do not interfere with the later gravimetric analysis of the deposit. The position of hydrogen in the middle of the electromotive series permits some major divisions. For instance, copper, mercury, gold, and silver can be deposited from moderately strong acid solutions without liberating much hydrogen. The phenomenon of overvoltage makes it possible to deposit zinc and cadmium from weak acids. In the case of nickel and cobalt, a deposit is obtained only in alkaline solutions, since the hydrogen evolution in acid solutions goes on at a lower potential than the deposition of these metals. Unwanted end-products of the electrode reactions which might react with the deposits are removed from the solution by so-called addition reagents. For example, urea is added to remove any nitrous acid formed from nitric acid at the cathode; toluene is added to remove chlorine gas formed by the oxidation of chloride ions at the anode.

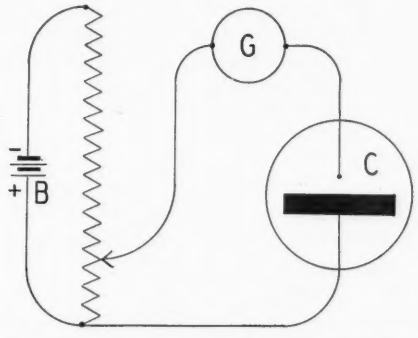

FIGURE 4.—SCHEME OF CIRCUIT USED FOR POLAROGRAPHIC ANALYSES

The Polarographic Method.—In this method, electrolyses are combined with simultaneous potential measurements. However, both procedures differ fundamentally from those described in the two previous chapters. Distinct from the electrolytic method, the polarographic electrolyses leave the body of the solution practically unaltered because they are carried out with very small electrodes and are always of short duration. Also differing from the potentiometric method, the potential, E, of the polarized small electrode is obtained while current is flowing. This is done with the help of Ohm's law by using the following equation:

$$E = E_r + V - IR \qquad (3)$$

where V is the known applied voltage, I the corresponding current (negative if cathodic, positive if anodic), R the resistance of the circuit, and E_r the known potential of the non-polarizable reference electrode which is in series with the small polarizable electrode.

The setup is sketched in Figure 4. From some outside source, B, a known voltage is applied to the cell C,

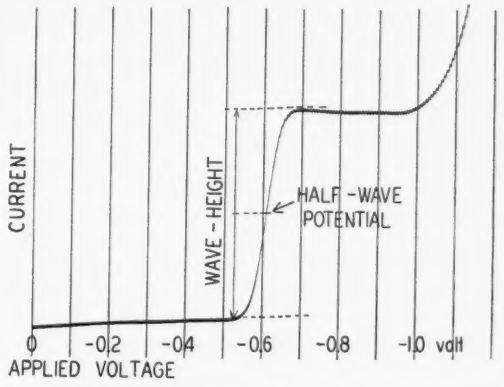

FIGURE 5.—TYPICAL POLAROGRAM
Air-free solution of 0.001 M $CdSO_4$ in 0.1 M $CoCl_2$ buffered at pH 5

consisting of one small easily polarizable and one large non-polarizable electrode. The potential of the latter is known and serves as reference. The applied voltage is gradually changed and the current corresponding to each voltage is measured by means of a galvanometer, G. An increase in current will be noted when the applied voltage has reached a value at which some material present in the solution will react. This increase in current will continue with increasing voltage but will reach a limit when the electrode potential attains such a value that all the reacting material which reaches the electrode in unit time is electrolyzed. Thus, under suitable conditions, a graph (polarogram) of the observed current against the applied voltage will show an S-shaped curve (Figure 5). The height of this curve (wave height) is a function of the concentration of the reacting material, and the potential corresponding to the point of inflection of the curve (half-wave potential) is characteristic of the nature of the reacting material. This is the basis of quantitative and qualitative polarographic analysis.

If we compare such a polarographic curve with a potentiometric titration curve (Figure 2), we find that they are practically identical. There, too, the midpoint of the curve gives us E_0, the characterizing potential of the oxidation–reduction system. Also at the endpoint of the titration, the potential is poorly defined and changes rapidly. Yet the conditions under which these curves are obtained are quite different. In the polarographic method we deal only with the electrode–solution interface, which is a thin layer of solution in immediate contact with the electrode. Instead of changing the

whole of the solution by adding a titrating agent, we change only the ratio of oxidant to reductant present in the interface. This is done by means of the electric current, *i. e.*, by the direct addition or removal of electrons, and the resulting change is measured by observing the potential which the electrode has acquired in this system. This is based on the assumption—which seems to be verified by experiment—that the equilibrium between electrode and interface, involving the transfer of electrons, is established immeasurably fast, while the attainment of equilibrium between the interface and the rest of the solution, involving the migration and the diffusion of ions, atoms, and molecules, takes a relatively long time. The influence of migration can be neglected if an excess of an indifferent salt is added to the solution. Thus only diffusion to and from the interface is left as the most decisive factor in polarographic analyses, aside from the possible mechanical movement of material to the electrode by stirring. In order to repeat and to correlate different experiments, it is essential that an electrode be used which permits a perfect reproduction of conditions at the interface.

By far the most satisfactory electrode for this purpose is a slowly growing drop of mercury. The use of this electrode was long delayed, undoubtedly because of the experience with dropping electrodes with a very rapid flow of mercury, which were used in attempts to find an absolute potential for a standard of reference. Kučera introduced a slowly dropping mercury electrode for the study of surface tension by the drop-weight method. Heyrovský was the first to make use of this electrode for electrolyses, which led to the development of the polarographic method. It has the following advantages which cannot be matched by any other electrode: (1) its surface is reproducible, smooth, and continually renewed; (2) the surface area can be calculated from the weight of the drops; (3) mercury amalgamates with most metals; (4) the value of the overvoltage of hydrogen is highest on mercury so that much work can be done in acid solutions without interference from the evolution of hydrogen.

It has been found that solid electrodes made from different metals can also be used for these polarographic studies if their surface is renewed by some mechanical device. Even without this mechanical renewal of their surface, they are suitable for studies of systems in which oxidant as well as reductant remains in solution. However, analyses made with solid electrodes are usually less accurate than those made with dropping mercury, because the surface of a solid electrode is never as smooth as that of liquid mercury and is usually covered with a thin film of oxide or adsorbed material. Furthermore, it is difficult to reproduce perfectly any mechanical agitation of the solution when the electrodes are scraped or rotated, or when the solution is made to flow past a stationary electrode. Solid electrodes will, therefore, only play an important role for polarographic analyses which are outside the potential range of the dropping mercury electrode, or in studies where not much accuracy is required.

The polarographic method has found applications in a great many fields. Every reversible organic and inorganic oxidation–reduction system falls within its scope. Curves similar to those in Figure 3 and with similar limitations are obtained in two-step oxidations and reductions, and in simultaneous analyses of two reactive components in solution. Even irreversible systems give reproducible curves that can be used for analytical purposes. Finally, several strictly empirical procedures have been developed which are used in blood analyses; they show promise of giving us valuable information in combination with electrophoretic analyses. The necessary apparatus, details of the procedures, and examples of their application will be given in subsequent articles.

A special application of the polarographic method is the determination of one component of a solution by means of a *fixed* specific potential. For instance, the concentration of oxygen in solution can often be obtained directly from the deflection of a galvanometer in a previously calibrated setup. A more common application is in precipitation reactions in which the current at a fixed potential decreases to zero or to some other limiting value when the endpoint is reached. The curves obtained by plotting current against the volume of added reagent closely resemble the conductometric titration curves shown in Figure 1. It is usually possible in these titrations to extrapolate to zero or to a minimum current from a few experimental points. Also sometimes two different components can be titrated simultaneously. These so-called *polarometric titrations* are extremely simple and fast; they will undoubtedly become very popular when enough procedures have been worked out on the basis of complete polarographic analyses. Further details and illustrations by means of examples will be given in subsequent articles.

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An Elementary Formulation of Statistical Mechanics

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INTRODUCTION

IT MUST be clear to the most casual reader that many aspects of the current chemical literature are being formulated more and more in the language of statistical mechanics. It is also apparent to a teacher that statistical mechanics is regarded by most undergraduates as well as many graduate students as a very mysterious subject. We believe that this unfortunate situation is often the result of an unnecessarily involved presentation of the subject. The purpose of this article is to show that any student who has the training requisite for the elementary course in physical chemistry cannot only understand but can use statistical mechanics in all rate and equilibrium problems.

THE BOLTZMANN DISTRIBUTION LAW

The fundamental equation of statistical mechanics is the Boltzmann law of energy distribution. To derive this law, we consider a system of s distinguishable harmonic oscillators in equilibrium with a system, A, which may or may not be another harmonic oscillator. From quantum mechanics we know that an harmonic oscillator can absorb energy only in integral multiples of $h\nu$, where ν is the fundamental frequency of the oscillator and h is Planck's constant. We now wish to determine the probability that A have an amount of energy, ϵ, if the total amount of energy available is E. In order to calculate this probability we make the following assumption:

Any particular way of distributing the energy, E, between the s oscillators and system A has the same *a priori* probability as any other way of distributing the energy. Thus the probability of the energy, ϵ, being present in system A in a uniquely specifiable way is just proportional to the number of ways the energy $(E - \epsilon)$ can be distributed among the s distinguishable oscillators. This simple assumption of equal *a priori* probability for the various ways of distributing the energy E (or an equivalent assumption) is always either implicitly or explicitly made in every formulation of statistical mechanics.

In Figure 1, each of the points represents a different way of distributing the energy $(E - \epsilon)$ *or less* among two oscillators. If $(E - \epsilon)$ *is large*, the number of different ways of distributing the energy $(E - \epsilon)$ or less is equal to the area of the triangle with sides $(E - \epsilon)$, or

$$N = \frac{(E - \epsilon)^2}{2!}$$

Similarly, for the case of three oscillators, the number of different ways of distributing the energy $(E - \epsilon)$ or less is equal to the volume of the pyramid with edges $(E - \epsilon)$, or

$$N = \frac{(E - \epsilon)^3}{3!}$$

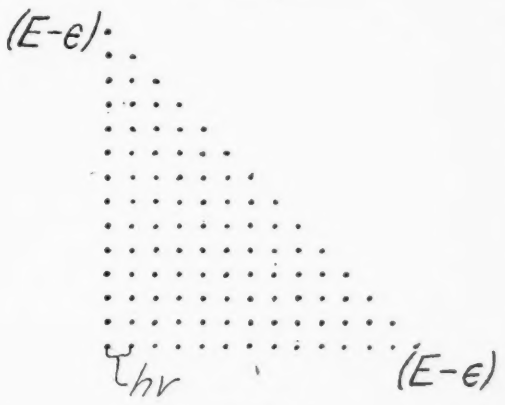

FIGURE 1

For s oscillators we find in the same way that

$$N = \frac{(E - \epsilon)^s}{s!}$$

Since any point on the surface of this s-dimensional volume represents a different way of distributing the energy $(E - \epsilon)$, the number of ways in which this energy can be distributed among the s oscillators is equal to the surface area of this volume $= -\frac{dN}{d\epsilon}$.

$$-\frac{dN}{d\epsilon} = s\,\frac{(E-\epsilon)^{s-1}}{s!} = \frac{sE^{s-1}}{s!}\left(1 - \frac{\epsilon}{E}\right)^{s-1} = a'\left(1 - \frac{\epsilon}{E}\right)^{s-1}$$

According to our assumption,

$$P(\epsilon) = c\,\frac{dN}{d\epsilon}$$

or

$$P(\epsilon) = a\left(1 - \frac{\epsilon}{E}\right)^{s-1}$$

If E and s are large, we may write

$$E = sE_{av.}$$

where $E_{av.}$ is the average energy per oscillator. Making this substitution, we have

$$P(\epsilon) = a\left(1 - \frac{\epsilon}{sE_{av.}}\right)^{s-1}$$
$$= a\left\{1 - \frac{(s-1)}{s}\left(\frac{\epsilon}{E_{av.}}\right) + \frac{(s-1)(s-2)}{2!s^2}\left(\frac{\epsilon}{E_{av.}}\right)^2 - \frac{(s-1)(s-2)(s-3)}{3!s^3}\left(\frac{\epsilon}{E_{av.}}\right)^3 + \cdots\right\}$$

If s is a very large number, this becomes

$$P(\epsilon) = a\left\{1 - \frac{\epsilon}{E_{av.}} + \frac{1}{2!}\left(\frac{\epsilon}{E_{av.}}\right)^2 - \frac{1}{3!}\left(\frac{\epsilon}{E_{av.}}\right)^3 + \cdots\right\}$$

$$= ae^{-\frac{\epsilon}{E_{av.}}}$$

This is the fundamental equation upon which all our subsequent discussions will be based. Let us denote by ϵ_n the energy of A in the nth state. Since the probability that A be in *some* state is unity, we have

$$\sum_n P(\epsilon_n) = \sum_n ae^{-\frac{\epsilon_n}{E_{av.}}} = 1$$

or

$$a = \frac{1}{\sum_n e^{-\frac{\epsilon_n}{E_{av.}}}}$$

If A is a harmonic oscillator,

$$\epsilon_n = nh\nu$$

and

$$P(\epsilon_n) = \frac{e^{-\frac{nh\nu}{E_{av.}}}}{\sum_n e^{-\frac{nh\nu}{E_{av.}}}}$$

A crystal composed of N atoms may be treated as a set of $3N$ harmonic oscillators. At high temperatures, the specific heat of a crystal, by the familiar law of Dulong and Petit, is $3R$, which is equivalent to a specific heat of k per oscillator. We may thus evaluate $E_{av.}$ in the above equations by calculating the high temperature specific heat of an oscillator. The total energy E_1 will be given by the sum of the energy of each state times the probability that the oscillator be in that state, *i. e.*,

$$E_1 = \sum_n nh\nu\, P(nh\nu) = \frac{\sum_n nh\nu\, e^{-\frac{nh\nu}{E_{av.}}}}{\sum_n e^{-\frac{nh\nu}{E_{av.}}}}$$

This may be written as

$$E_1 = -\frac{d}{d\left(\frac{1}{E_{av.}}\right)} \log\left(\sum_n e^{-\frac{nh\nu}{E_{av.}}}\right)$$

$$= -\frac{d}{d\left(\frac{1}{E_{av.}}\right)} \log\left(1 + e^{-\frac{h\nu}{E_{av.}}} + \left(e^{-\frac{h\nu}{E_{av.}}}\right)^2 + \left(e^{-\frac{h\nu}{E_{av.}}}\right)^3 + \cdots\right)$$

$$= -\frac{d}{d\left(\frac{1}{E_{av.}}\right)} \log \frac{1}{\left(1 - e^{-\frac{h\nu}{E_{av.}}}\right)}$$

$$= \frac{h\nu}{e^{\frac{h\nu}{E_{av.}}} - 1} = \frac{h\nu}{\frac{h\nu}{E_{av.}} + \frac{1}{2!}\left(\frac{h\nu}{E_{av.}}\right)^2 + \frac{1}{3!}\left(\frac{h\nu}{E_{av.}}\right)^3} + \cdots$$

If $E_{av.} >> h\nu$, which is the case at high temperatures, we have

$$E_1 = \frac{h\nu}{\frac{h\nu}{E_{av.}}} = E_{av.}$$

The specific heat is equal to

$$\frac{dE_1}{dT} = \frac{dE_{av.}}{dT} = k$$

Therefore

$$E_{av.} = kT + c$$

where c is a constant.
Since the energy must be zero when $T = 0$, we see from the relation

$$E_1 = \frac{h\nu}{e^{\frac{h\nu}{kT + c}} - 1}$$

that c must be zero. Our fundamental equation thus becomes

$$P(\epsilon_i) = \frac{e^{-\frac{\epsilon_i}{kT}}}{\sum_i e^{-\frac{\epsilon_i}{kT}}}$$

where $P(\epsilon_i)$ is the probability that any molecular system have the energy ϵ_i in a single state. If the energy can be taken up in more than one way, the probability of having the energy will be increased by this factor. In the general case we could write

$$P(\epsilon_i) = \frac{g_i e^{-\frac{\epsilon_i}{kT}}}{\sum_i g_i e^{-\frac{\epsilon_i}{kT}}}$$

where g_i, the "statistical weight," is the number of ways in which the energy ϵ_i can be absorbed.

If the system A in the above treatment were in equilibrium with a set of s particles which could take up energy according to the law

$$\epsilon' = cn^m$$

where c is a constant and n is an integer, then the same treatment as we used for the case of harmonic oscillators would show that the number of ways of distributing the energy $(E - \epsilon)$ or less is

$$N = b\left(1 - \frac{\epsilon}{E}\right)^{\frac{s}{m}}$$

In this case we would have

$$P(\epsilon) = c\frac{dN}{d\epsilon} = b'\frac{s}{m}\left(1 - \frac{\epsilon}{E}\right)^{\frac{s}{m}-1} = a\left(1 - \frac{\epsilon}{sE_{av.}}\right)^{\frac{s}{m}-1}$$

$$= a\left(1 - \frac{\epsilon}{\frac{s}{m}(mE_{av.})}\right)^{\frac{s}{m}-1} = ae^{-\frac{\epsilon}{mE_{av.}}}$$

But we know that

$$P(\epsilon) = ae^{-\frac{\epsilon}{kT}}$$

so that

$$mE_{av.} = kT$$

or

$$E_{av.} = \frac{kT}{m}$$

and the corresponding specific heat is k/m. For a translational degree of freedom the specific heat is $k/2$, so that we conclude that translational energy is absorbed according to the law $\epsilon = cn^2$. We have seen that the probability of a system being in a particular state is

$$P = ae^{-\frac{\epsilon}{kT}}$$

Then the chance that it shall be in the group of translational states with quantum numbers between n_x and $n_x + dn_x$, n_y and $n_y + dn_y$, n_z and $n_z + dn_z$ is

$$P = ae^{-\frac{\epsilon}{kT}}\, dn_x\, dn_y\, dn_z$$

Using the relations

$$\epsilon_x = c_x n_x^2 = \frac{m}{2}V_x^2, \epsilon_y = c_y n_y^2 = \frac{m}{2}V_y^2, \epsilon_z = c_z n_z^2 = \frac{m}{2}V_z^2$$

we see that the probability that a molecule have components of velocity in the x, y, and z directions between V_x and $V_x + dV_x$, V_y and $V_y + dV_y$, V_z and $V_z + dV_z$ is

$$P = a\left(\frac{m^3}{8c_x c_y c_z}\right)^{1/2} e^{-\frac{m}{2kT}(V_x^2+V_y^2+V_z^2)}\, dV_x\, dV_y\, dV_z$$

Making the substitution

$$V^2 = V_x^2 + V_y^2 + V_z^2$$

we may write

$$P = a'e^{-\frac{mV^2}{2kT}} V^2 dV$$

The fraction of molecules with velocities between V and $V + dV$ is therefore

$$\frac{\delta N}{N} = \frac{e^{-\frac{mV^2}{2kT}}V^2 dV}{\int_0^\infty e^{-\frac{mV^2}{2kT}}V^2 dV} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mV^2}{2kT}} V^2 dV$$

which is the Maxwell-Boltzmann law of distribution of molecular velocities. The average velocity of the molecules is

$$\overline{V} = \int_0^\infty V\frac{\delta N}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-\frac{mV^2}{2kT}} V^3 dV = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

Since the energy $\epsilon = {}^1/_2 mV^2$, we may obtain the expression for the fraction of molecules with energies between ϵ and $\epsilon + d\epsilon$ by transforming the equation for the fraction having a velocity between V and $V + dV$. The result is

$$\frac{\delta N}{N} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2} e^{-\frac{\epsilon}{kT}}\epsilon^{1/2}\, d\epsilon$$

The average translational energy, as we already know, is

$$\bar{\epsilon} = \int_0^\infty \epsilon\frac{\delta N}{N} = 2\pi\left(\frac{1}{\pi kT}\right)^{3/2}\int_0^\infty e^{-\frac{\epsilon}{kT}}\epsilon^{3/2}\, d\epsilon = \frac{3}{2}kT$$

RELATION OF STATISTICAL MECHANICS TO THERMODYNAMICS

The quantity $f = \sum_i e^{-\frac{\epsilon_i}{kT}}$ is called the partition function. We will now give an interpretation of the various thermodynamic functions in terms of the partition function, which will enable us to calculate the values of the thermodynamic functions directly from our knowledge of the energy levels of a particular system. Consider the case of equilibrium between two molecules A and B. The energy levels of the system may be represented diagramatically as in Figure

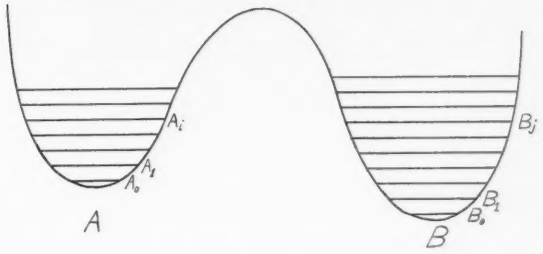

FIGURE 2

2. The probability that the system will be in the state A_i will be

$$P = ae^{-\frac{\epsilon_{A_i}}{kT}}$$

The probability that the system will be in the state B_j will be

$$P = ae^{-\frac{\epsilon_{B_j}}{kT}}$$

Therefore,

$$\frac{\text{Probability of being in a state corresponding to } A}{\text{Probability of being in a state corresponding to } B} =$$

$$\frac{\text{Number of } A \text{ molecules}}{\text{Number of } B \text{ molecules}} = \frac{a\sum_i e^{-\frac{\epsilon_{A_i}}{kT}}}{a\sum_j e^{-\frac{\epsilon_{B_j}}{kT}}} = \frac{f_A}{f_B}$$

For the relation between the standard free energy change and the equilibrium constant of a reaction we have

$$\Delta F^\circ = -RT\log K_c.$$

Let us consider the reaction

$$N_2 + 3H_2 = 2NH_3$$

$$2F^\circ_{NH_3} - 3F^\circ_{H_2} - F^\circ_{N_2} = -RT\log\frac{[NH_3]^2}{[H_2]^3[N_2]}$$

$$= -RT\left\{\log\left(\frac{N_{NH_3}}{V}\right)^2 - \log\left(\frac{N_{H_2}}{V}\right)^3 - \log\left(\frac{N_{N_2}}{V}\right)\right\}$$

From previous considerations, we know that

$$N_{NH_3}:N_{H_2}:N_{N_2}::f_{NH_3}:f_{H_2}:f_{N_2}$$

Therefore

$$2F^\circ_{NH_3} - 3F^\circ_{H_2} - F^\circ_{N_2} = -RT\left\{\log\left(\frac{f_{NH_3}}{V}\right)^2 - \log\left(\frac{f_{H_2}}{V}\right)^3 - \log\left(\frac{f_{N_2}}{V}\right)\right\}$$

By identifying terms on each side of the equation which are functions of a particular molecular species only, we have

$$3F^\circ_{H_2} = -RT\left\{\log\left(\frac{f_{H_2}}{V}\right)^3 + \alpha\right\}$$

$$F^\circ_{N_2} = -RT\left\{\log\left(\frac{f_{N_2}}{V}\right) + \beta\right\}$$

$$2F^\circ_{NH_3} = -RT\left\{\log\left(\frac{f_{NH_3}}{V}\right)^2 + \alpha + \beta\right\}$$

By the manner in which the constants α and β appear, we see that α can be a function of the hydrogen atom only, and β can be a function of the nitrogen atom only. These functions will cancel out in any discussion of chemical equilibrium, and for convenience may be set equal to zero. We now have as a general expression relating standard free energy to the partition function

$$F^\circ = -RT\log\left(\frac{f}{V}\right)$$

The free energy will be given by the relation

$$F = F^\circ + RT\log\left(\frac{N}{V}\right)$$

$$= -RT\left\{\log\left(\frac{f}{V}\right) - \log\left(\frac{N}{V}\right)\right\} = -RT\log\left(\frac{f}{N}\right) = -kT\log\left(\frac{f}{N}\right)^N$$

The Helmoltz free energy can be expressed in terms of the partition function in the following manner.

$$A = F - PV = F - RT = -kT\{\log f^N - N\log N + N\}$$

$$= -kT\left\{\log f^N - N\log\left(\frac{N}{e}\right)\right\} = -kT\{\log f^N - \log(N!)\}$$

$$= -kT\log\frac{f^N}{N!}$$

In the discussion above we have derived expressions for E, F, and A in terms of the partition function f. Other thermodynamic functions may now be expressed in terms of the partition function by means of the various relations between them. The entropy and pressure are determined as follows. From the equation

$$A = E - TS$$

we have

$$dA = dE - TdS - SdT$$

Also,

$$dQ = TdS = dE + pdV$$

Combining these two equations, we have

$$dA = -SdT - pdV$$

Therefore

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

The latter equation is the thermodynamic equation of state.

For any given molecule, translational, rotational, vibrational, and electronic energies must be considered in evaluating the partition function. Each energy level may be identified by assigning to it four quantum numbers, one for each type of energy. The partition function will then be

$$f = \sum_{t,r,v,e} e^{-\frac{E_{t,r,v,e}}{kT}}$$

where the summation is over all possible combinations of quantum numbers. To a good approximation the energy may be expressed as a sum of the energies of each type of motion, and we may write

$$E_{t,r,v,e} = E_t + E_r + E_v + E_e$$

When the energy is expressed in this form, the partition function becomes

$$f = \sum_{t,r,v,e} e^{-\frac{E_t + E_r + E_v + E_e}{KT}}$$

$$= \sum_t e^{-\frac{E_t}{kT}} \sum_r e^{-\frac{E_r}{kT}} \sum_v e^{-\frac{E_v}{kT}} \sum_e e^{-\frac{E_e}{kT}} = f_t f_r f_v f_e$$

The partition function may be evaluated for any given molecule if the energy levels are known either from spectroscopic data or from a quantum mechanical treatment of the molecule.

(1) Partition function for translational motion

For a particle of mass, m, moving in a box with edges of length a, b, c, the energy levels are

$$E_{p,q,r} = \frac{h^2}{8m}\left\{\frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2}\right\}$$

where p, q, r, are integers. The partition function is

$$f_t = \sum_{p=1}^{\infty} e^{-\frac{p^2h^2}{8ma^2kT}} \sum_{q=1}^{\infty} e^{-\frac{q^2h^2}{8mb^2kT}} \sum_{r=1}^{\infty} e^{-\frac{r^2h^2}{8mc^2kT}}$$

Since the quantities $\frac{h^2}{8ma^2kT}$, $\frac{h^2}{8mb^2kT}$, $\frac{h^2}{8mc^2kT}$ are all much less than unity under ordinary conditions of temperature and volume, the summations may be replaced by integrations. Since

$$\int_0^\infty e^{-\frac{p^2h^2}{8ma^2kT}}\,dp = \frac{(2\pi mkT)^{1/2}a}{h}, \text{ etc.,}$$

$$f_t = \frac{(2\pi mkT)^{3/2}}{h^3}abc = \frac{(2\pi mkT)^{3/2}}{h^3}V$$

(2) Partition function for rotational motion

For a linear molecule with moment of inertia I, the rotational energy levels are

$$J(J+1)\frac{h^2}{8\pi^2 I}$$

where there are $2J + 1$ states for each value of the energy.

$$f_r = \sum_{J=0}^{\infty} (2J+1)\, e^{-\frac{J(J+1)h^2}{8\pi^2 IkT}}$$

At high temperatures, we may again replace the sum by an integral, and find

$$f_r = \frac{8\pi^2 IkT}{h^2}$$

In the case in which the two ends of the molecule are identical, the quantum mechanical treatment shows that only alternate values of the quantum number J are allowed. In evaluating the partition function we must then sum over half the levels only, obtaining

$$f_r = \frac{8\pi^2 IkT}{2h^2}$$

In general we write for a linear molecule

$$f_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

where the symmetry number σ is 2 if both ends of the molecule are identical and 1 otherwise; that is, σ is the number of equivalent ways of orienting the molecule in space.

For a non-linear molecule with principal moments of inertia A, B, C, a similar treatment shows that the partition function is

$$f_r = \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}$$

σ depends upon the symmetry of the molecule and is again determined by counting the number of equivalent ways of orienting the molecule in space; for example, for H_2O, $\sigma = 2$; for NH_3, $\sigma = 3$; for C_2H_4, $\sigma = 4$; for CH_4, $\sigma = 12$; for C_6H_6, $\sigma = 12$.[1]

(3) *Vibrational partitional function*

A molecule consisting of n atoms has $3n - 6$ vibrational degrees of freedom if it is non-linear, and $3n - 5$ if it is linear. Each vibrational degree of freedom may be considered as an harmonic oscillator, for which we have already derived the partition function

$$f_v = \frac{1}{1 - e^{-\frac{h\nu}{kT}}}$$

For i vibrational degrees of freedom, the vibrational partition function is $\prod_i \left(\frac{1}{1 - e^{-\frac{h\nu_i}{kT}}}\right)$. The frequencies ν_i may be obtained from an analysis of the infra-red and Raman spectra of the molecule.

(4) *Electronic partition function*

The electronic partition function must be calculated directly from the relation

$$f_e = \sum_e g_e e^{-\frac{E_e}{kT}}$$

using the observed values of the electronic energy levels. In most molecules the excited states are too high in energy to contribute to the partition function at ordinary temperatures. As the ground state is non-degenerate for most molecules, the electronic partition function is usually unity.

For a non-linear molecule composed of n atoms we have the partition function

$$f = \left\{\frac{(2\pi mkT)^{3/2}}{h^3} V\right\}\left\{\frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{\sigma h^3}\right\} \times \left\{\prod_{i=7}^{i=3n}\left(1 - e^{-\frac{h\nu_i}{kT}}\right)^{-1}\right\}$$

The partition function is thus a function of the mass, moments of inertia, vibrational frequencies, and symmetry of the molecule, as well as the volume and temperature, and can be evaluated as soon as these quantities are determined.

We can calculate the pressure of a gas composed of such molecules as follows:

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\frac{\partial}{\partial V}\log\frac{f^N}{N!} = NkT\frac{\partial}{\partial V}\log f = \frac{NkT}{V}$$

If we include in our energy terms the potential energy of interaction between molecules, we will get an additional term in our translational partition function. For example, if in the translational partition function for a perfect gas $\frac{(2\pi mkT)^{3/2}}{h^3}V$ we replace V by $(V - b)$ and multiply by $e^{\frac{a}{VRT}}$, we have the partition function for a van der Waals' gas, as may be seen by calculating the pressure.

For solids and liquids the translational and rotational partition functions will be replaced by vibrational partition functions in which the frequencies are functions of volume and temperature; and there will be a term $e^{-\frac{E(V,T)}{RT}}$ analogous to the term $e^{\frac{a}{VRT}}$ for a van der Waals' gas. However, having explicitly introduced these new partition functions, all the thermodynamic properties are calculable in exactly the same way as for a gas.

THE THEORY OF REACTION RATES

Any chemical reaction $A + B \longrightarrow C + D$ may be described in the following terms. For the system $A + B$ we have a certain potential energy surface with a definite set of energy levels, and for the system $C + D$ we have a different potential energy surface with different energy levels. The two potential energy surfaces join smoothly, and there will in general be one way of going from the one to the other which requires less energy than any other path. Pictorially, we may say that the complete potential energy surface is represented by two mountain valleys with a pass connecting them. If we take a cross section of the surface through the pass, the result is as illustrated in

[1] It is of some interest to note that in the partition function for N molecules we have the factor $N!$ occurring in the denominator. This is the number of indistinguishable configurations of N identical molecules in space and is really a symmetry number also. In quantum mechanics one sees that it has precisely the same significance as the other symmetry numbers, *i. e.*, an interchange of positions of identical particles does not lead to a new energy state but is only one of the phases of a single state. This last experimental fact is usually called the Pauli Exclusion Principle.

Figure 3. At the top of the pass we have the molecules $A + B$ combined into a single molecule which may be treated in the same manner as any ordinary molecule, except that we recognize that motion along the bottom of the pass leads to dissociation either into $A + B$ or into $C + D$. If we know the shape of the potential energy surface in the region of the pass, and the coordinates of the atoms in the combined molecule $\overline{AB}$ (the activated complex) we can calculate a partition function for this complex in the usual manner.

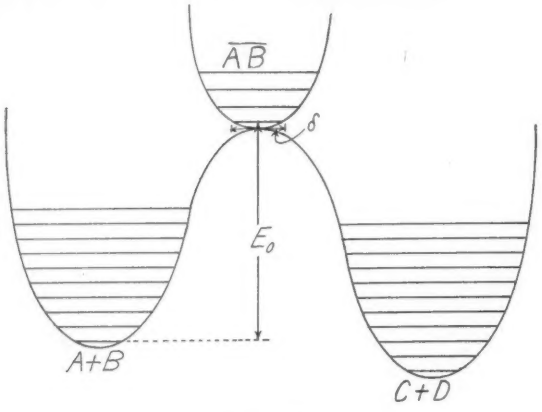

FIGURE 3

The rate of reaction per unit volume is equal to the concentration of $\overline{AB}$ complexes times the rate at which they decompose into $C + D$, that is, by the rate at which they move along the reaction path in the direction of $C + D$. Since the complexes $\overline{AB}$ are in equilibrium with the molecules $A + B$

$$\frac{C_{\overline{AB}}}{C_A C_B} = \frac{\left(\frac{N_{\overline{AB}}}{V}\right)}{\left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right)} = \frac{\left(\frac{f_{\overline{AB}}}{V}\right)}{\left(\frac{f_A}{V}\right)\left(\frac{f_B}{V}\right)}$$

We will now write

$$f_{\overline{AB}} = f'_{\overline{AB}}\, e^{-\frac{E_0}{kT}}$$

where $f'_{\overline{AB}}$ is the partition function for the activated complex with the energy at the top of the barrier taken as zero. We also write

$$f'_{\overline{AB}} = f^{\ddagger}_{\overline{AB}} \frac{(2\pi m_{\overline{AB}} kT)^{1/2}\delta}{h}$$

where $f^{\ddagger}_{\overline{AB}}$ is the partition function for all degrees of freedom except that for motion along the reaction path for which we have written the translational partition function for a particle of mass $m_{\overline{AB}}$ in a one-dimensional box of length δ.

The complex $\overline{AB}$ is as likely to be moving in the backward as in the forward direction; the rate at which they decompose into $C + D$ is given by

$$\frac{1}{2}\frac{(\text{average velocity along } \delta)}{\delta} = \frac{\overline{P}}{2m_{\overline{AB}}\delta}$$

where P, the average momentum, is given by the equation

$$\overline{P} = \frac{\int_0^\infty e^{-\frac{p^2}{2m_{\overline{AB}}kT}}\, p\,dp}{\int_0^\infty e^{-\frac{p^2}{2m_{\overline{AB}}kT}}\, dp} = \frac{(2m_{\overline{AB}}kT)^{1/2}}{\pi^{1/2}}$$

The rate of reaction is

$$R = C_{\overline{AB}} \cdot \frac{(2m_{\overline{AB}}kT)^{1/2}}{2\pi^{1/2}m_{\overline{AB}}\delta} = C_A C_B \frac{kT}{h} \frac{\left(\frac{f^{\ddagger}_{\overline{AB}}}{V}\right)}{\left(\frac{f_A}{V}\right)\left(\frac{f_B}{V}\right)} e^{-\frac{E_0}{kT}}$$

It is possible that not every complex which crosses the pass will actually produce the reactants, as it might return to the other side before decomposing. If κ is the probability that a complex which has crossed the barrier produces the reactants, then the proper expression for the rate is

$$R = \kappa C_A C_B \frac{kT}{h} \frac{\left(\frac{f^{\ddagger}_{\overline{AB}}}{V}\right) e^{-\frac{E_0}{kT}}}{\left(\frac{f_A}{V}\right)\left(\frac{f_B}{V}\right)}$$

Let us calculate the rate of a reaction in which two atoms unite to form a diatomic molecule $A + B \longrightarrow \overline{AB} \longrightarrow AB$.

$$\frac{f_A}{V} = \frac{(2\pi m_A kT)^{3/2}}{h^3} \qquad \frac{f_B}{V} = \frac{(2\pi m_B kT)^{3/2}}{h^3}$$

$$\frac{f^{\ddagger}_{\overline{AB}}}{V} = \frac{(2\pi[m_A + m_B]kT)^{3/2}}{h^3} \frac{8\pi^2 \frac{m_A m_B}{m_A + m_B} r^2_{\overline{AB}}\, kT}{h^2}$$

There is no vibrational term in $f^{\ddagger}_{\overline{AB}}$, as this degree of freedom corresponds to motion along the reaction path. The rate is

$$R = \kappa C_A C_B\, kT \frac{(2\pi[m_A + m_B]kT)^{3/2} 8\pi^2 \frac{m_A m_B}{m_A + m_B} r^2_{\overline{AB}}\, kT}{(2\pi m_A kT)^{3/2}\,(2\pi m_B kT)^{3/2}} e^{-\frac{E_0}{kT}}$$

$$= \kappa C_A C_B \cdot 2r^2_{\overline{AB}} \left(\frac{2\pi kT}{\mu}\right)^{1/2} e^{-\frac{E_0}{kT}}$$

where

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

In this simple case the expression for the rate is identical with the results of the collision theory if we identify the collision diameter with $r_{\overline{AB}}$ and the steric factor with κ. This is the simplest way of obtaining the usual collision theory rate expression.

The preceding arguments thus lay the entire foundation for the treatment of all equilibrium and rate processes.

Lecture Experiments in General Chemistry[1]

VI. The Liquefaction and Fractionation of Air

VII. The Liquefaction and Fractionation of Natural Gas

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THE liquefaction and fractionation of gases present considerable difficulties to the lecturer when an attempt is made actually to demonstrate the principles and processes involved. The two methods presented in this paper overcome most of these difficulties and make this type of experiment just another routine lecture demonstration. The apparatus for the liquefaction of air is applicable to any liquefaction where an efficient condenser is necessary and where visible condensation is desirable, while the second is applicable to liquids which require efficient fractionation and freeze at the temperature of the refrigerant.

VI. THE LIQUEFACTION AND FRACTIONATION OF AIR

In most courses in general chemistry, students are told that when air is cooled sufficiently and enough pressure is applied it becomes a liquid. This seems rather simple to the student until he examines the diagram of the complex liquid air machine in his textbook. The student is also told that liquid air is fractionated to obtain the vast quantities of relatively pure nitrogen and oxygen used in commerce. Thus there seems to be need of some lecture demonstration of these facts.

In devising such a low temperature lecture demonstration one at once experiences the difficulty of having the apparatus fogged by moisture in the air. To avoid this, an insulated box with double-walled cellophane front, which can be filled with dry air, may be constructed. If a vacuum tube similar to that shown in Figure 1 is available, it is not necessary to use an insulated box. A simple pyrex condenser is built, as shown in Figure 1, in which to collect the liquid air. The jacket of the condenser is connected to a tube which is the intake for the cooling agent. Liquid nitrogen, which today is within easy shipping distance of almost every part of our country, is used as the cooling agent. Attached to the inner tube of the condenser is a rubber atomizer bulb, the intake of which is connected to a sodium hydroxide (pellet form) tube and a soda lime tube which remove the water and carbon dioxide from the air.

To operate this apparatus liquid nitrogen is slowly introduced into the outer jacket of the condenser until the apparatus is thoroughly cooled. Pressure is now applied by the hand bulb and drops of liquid air soon begin to fall into the receiving flask.

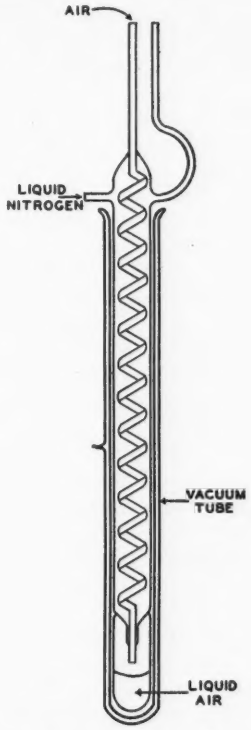

FIGURE 1.—APPARATUS FOR THE LIQUEFACTION AND FRACTIONATION OF AIR

When sufficient liquid has been collected the introduction of the cooling agent, liquid nitrogen, is ceased. The pressure bulb is disconnected from the condenser and a rubber tube attached in its place. As the liquid air begins to boil, the gas passes out through this rubber tube and samples are collected in test tubes. Testing these samples of gas from time to time with a glowing splint shows complete extinction of the splint by the first fractions and a bursting into flame in the later samples. This demonstration leaves little doubt in the mind about the possibility of obtaining a good separation of nitrogen and oxygen from liquid air.

By varying the cooling agent this apparatus may be used to liquefy a wide variety of gases.

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[1] Continuation of a previous paper by the same authors in J. CHEM. EDUC., **12**, 355 (1935).

Contribution from the Department of Chemistry, West Virginia University.

Some observations upon the color of liquid air and oxygen, condensed in this manner, as compared with samples of commercial liquid air and nitrogen, are of interest. Certain samples of commercial liquid nitrogen and liquid air were observed to have a much more intensely blue color than the liquids obtained by condensing atmospheric air or commercial (98 per cent) oxygen in the apparatus (Figure 1). It seems likely that this blue color, in many cases at least, is very largely due to some intensely blue liquid ozone rather than to liquid oxygen.

VII. THE CONDENSATION AND FRACTIONATION OF NATURAL GAS

A vacuum jacket is made from a pyrex Liebig condenser by evacuating and sealing the water jacket. Through the inner tube of this condenser there is a tube *H* with a bulb *D* attached. This bulb, made from a 10-cc. pipet, has an intake tube *A* for the gas sample. The tube *H* is wrapped at the points shown in Figure 2 with asbestos cord *C*. A large test tube *E* surrounds the bulb *D* to prevent freezing of the gas sample; this in turn is surrounded by the vacuum flask *F*.

The container *G* partially filled with liquid nitrogen makes the coldest point in the column *H*. The thermocouple *I*, located at this point, is connected by leads to a lecture table galvanometer. Rubber balloons are attached to *J* to collect the various fractions of the gas.

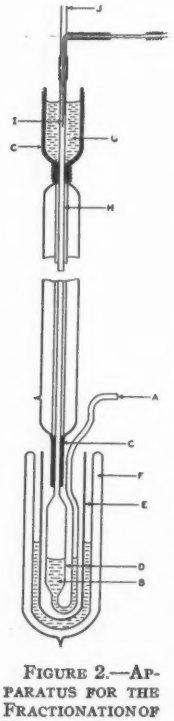


FIGURE 2.—APPARATUS FOR THE FRACTIONATION OF NATURAL GAS

To operate this apparatus, vacuum flask *F* is partially filled with liquid nitrogen, also container *G*. Tube *A* is attached to a source of natural gas and a slow stream passed through soda lime and dehydrite into the apparatus until the desired amount, about 10 cc., of liquid *B*, has condensed in the bulb. The major portion of the methane will have already distilled into the balloon. The nitrogen is now allowed to boil low in the vacuum flask *F*, or bulb *D*, containing the liquid natural gas, is partially removed from flask *F* in order to warm the liquid and start the distillation.

The galvanometer remains constant while the methane is distilling but there is a throw of the pointer when it is gone. The same is true with each fraction. By changing the balloon at *G* with each fraction the relative volumes of these may be shown. The last portion of liquid remaining in the flask is the gasoline content of the natural gas, namely, pentanes and higher-boiling compounds.

JOHN MERCER

(Frontispiece)

JOHN MERCER (1791–1866) was manager of the Oakenshaw Print Works in Accrington, near Manchester. In this capacity he acquired great technical experience. His name has been preserved in the term *mercerization*, though what we call the mercerizing process (the treatment by which a silk-like luster is given to cotton by the action of caustic soda solution on the stretched fibers) did not originate with him. Thomas and Prevost, in Krefeld, continued Mercer's work and invented the process in 1894. Basing his observations on experiments which go back to the year 1844, Mercer describes in his fundamental patent (1850) the increase of density and solidity as well as an increased receptivity for dyestuffs observed on cotton cloth treated with caustic soda.

In addition to his industrial activity, Mercer was engaged in a series of purely scientific problems. His biographer, Edward A. Parnell, in "The Life and Labours of John Mercer" (London, 1866) designates him as "The self-taught chemical philosopher." Thus he is, for instance, author of a treatise, "On relations of atomic weights of elements" (1858). Mercer plays an important part in the history of catalysis, being the first who had, in 1842, the opinion "that almost all instances of catalytic action may be reduced to feeble chemical affinity," a conception which was amplified to a special theory in 1848 by Sir Lyon Playfair (1819–1898). (Playfair became acquainted with Mercer in 1841 when he worked as a young chemist in Mercer's calico-printing factory; later he was professor of chemistry in Manchester and afterward at the Royal Institution of London.) Already, in 1830, Mercer had come upon catalytic phenomena while working on industrial experiments. He observed that the oxidation of the catechu dyestuff is accelerated by small quantities of manganese acetate and recognized that the manganese salt acts "as a bearer of oxygen from the air to the basis of the colouring matter." Likewise in 1841 he studied the decomposition of calcium hypochlorite and hypochlorous acid by cupric salts, considering this phenomenon as a catalytic action. The importance of mixed catalysts was already known to him. The merits of Mercer's work in catalytic research are well recognized in the book by A. Mittasch and E. Theis, "Von Davy und Döbereiner bis Deacon, ein halbes Jahrhundert Grenzflächenkatalyse" (Verlag Chemie, Berlin, 1932) ("From Davy and Döbereiner till Deacon, half a century of catalysis on boundary surfaces).

Pictures of Mercer are rare and the one used for the frontispiece represents a special historic curiosity; it is the reproduction of a photograph on cloth (shirting), blue-violet in color, which Mercer himself made by his own process. The original is part of the scientific inheritance of the grandfather of the writer, the famous dye chemist Heinrich Caro (1834–1910); it is now in the archives of the Deutsches Museum von Meisterwerken der Naturwissenschaft und Technik in Munich (Photograph No. 4119). Caro attached to the picture the following remarks in his own handwriting:

"This photograph of the famous English calico printer John Mercer (inventor of many print and dye processes and specially of the mercerizing process called after him, widely applied in recent time) was made by himself, by means of a light-sensitive (iron?) mordant of his invention, and subsequent dyeing in the madder bath. I received it at the beginning of the sixtieth year of the past century from John Dale, then my partner in Manchester, who had it as a present from John Mercer.[1] I do not know whether this photographic process has been published and applied."

—Contributed by Heinrich Rheinboldt
Universidade de São Paulo, Brazil

[1] H. Caro from 1859 to 1866 was associated with John Dale, manager of the Cornbrook Chemical Works, Roberts, Dale, and Company, in Manchester. Dale was one of the prominent industrialists of the time.

Simpler Weighing

GORHAM W. HARRIS Simmons College, Boston, Massachusetts

WISHING to get information about the systems of weighing in use for elementary quantitative analysis, the writer sent a short questionnaire to about fifty colleges and universities of larger size throughout the country. The forty-one replies received yielded the following statistics:

Method of weighing	*No. of colleges using*	*No. in elementary quantitative analysis*
Multiple swing, 3, 5, etc.	24	2890*
Double swing	7	1725
Double and single swing	5	855
Magnetic damping	4	355
Single swing only	1	50
Totals	41	5875*

* These totals are probably 200–300 larger in reality, as three institutions did not report the number of students.

In summary of the table: 24 institutions of the 41 reporting use the method of several swings for weighing, while 17 teach one or other of the time-saving methods listed. In the majority of colleges the multiple swing method is taught, but the number of students involved is only a little larger than that of those who are given one of the quicker methods. Only two of the nine institutions replying from west of the Mississippi were using the multiple swing method exclusively.

One reply, while stating that both double and single swing methods were taught, marked the multiple swing as the only one in actual use "for pedagogical reasons." The writer believes that the demands of logic and pedagogy can be well served if the multiple swing routine is taught and used a little, then replaced by a simpler technic.

Another response read: "Because of the large number of students taking our beginning course, and the fact that each one cannot have a balance for his exclusive use, it has not been found practicable to use the single deflection method." Each of our balances at Simmons College is used by five or more students, yet we have found it entirely feasible to use the one-swing procedure. Our experience may be of value to others in this very common situation.

It is carefully explained to the students that the pan arrests must have equal tension, as shown by the pointer remaining steadily at the center of the scale when the beam is released, and that the pan arrest button must be pushed in with a quick touch so that the pans will be released simultaneously and neither pan receive a greater impulse. The system has been in use at the college now for several years, and little or no more attention is required to keep the balances in order than was given in the past. More important, the results of analyses are quite as satisfactory as before, when multiple swings were used. The students serve an apprenticeship with multiple swings, and learn to appreciate the single deflection method when they adopt it a little later.

We have applied the term "swing point" to the spot at which the pointer stops at the end of its swing to the right, usually three or four spaces from the center. The student determines, when necessary, the zero swing point in starting a weighing and then, after two or three quick exploratory positions of the rider, computes the correct final position of the rider from the sensitivity of the balance.

It might be objected that when the balance has been set off-center for single deflection, it would be necessary to readjust it whenever one wishes to count multiple swings, as when calibrating weights to 0.01 mg. Nevertheless, adjustment of the nut at the end of the beam is not necessary in order to change from one system of weighing to the other, although that is the usual device for altering the center of swing. With its zero point at center, the balance can be made ready for one-swing weighing by placing on the left pan a one-milligram weight or a small piece of aluminum wire, as from a broken rider. This special adjusting weight may be stored in the weight box.

Whereas the single deflection procedure was hardly mentioned in textbooks of a decade ago, it gets adequate attention in several standard texts of recent years. First described briefly by Turner[1] in 1916 and more fully by Brinton[2] in 1919, it has been gradually gaining favor. Besides its speed, this technic has the advantage that there is but one value to remember or note—the swing point—and no computation is required as in finding the center of swing.

Another decided asset arises from the off-center condition of the balance. When the beam and pans are freed, the pointer moves without further assistance to the swing point. Fanning with the hand, often suggested in texts, causes delay until the air currents have subsided. Lifting the rider momentarily gives a satisfactory impulse, but is slow and clumsy in comparison with the quick automatic start with the off-center adjustment.

Since all one-swing readings are made at about the same point on the scale, one is less troubled by parallax than when reading both ends of a long swing, and a small lens gives easy magnification. Since a change in the rider position affects only one end of the pointer swing, the sensitivity of the balance measured by the swing point amounts to twice as much as when computed from the center of swings. The two-swing routine shows the same increased sensitivity when the sum of the swings is used.

[1] TURNER, "A rapid method of weighing," *Chemist-Analyst*, **16**, 21–2 (1916).

[2] BRINTON, "The single deflection method of weighing," *J. Am. Chem. Soc.*, **41**, 1151–5 (1919).

Obviously, this greater sensitivity does not indicate enhanced accuracy or precision. The writer timed and recorded zero points by each of the four methods reported in the questionnaire—one-, two-, and three-swing and magnetic damping. The readings by one and by two swings were about fifty per cent faster than the others (the single-swing the fastest), and more than twice as fast as five swings, but the precision of the quicker procedures was only about one-half that of the three-swing or damping. In no case, however, was the average deviation from the mean greater than a tenth of a space. Recent tests reported by Lin[3] and by Booth and Damerell[4] agree in finding the single deflection method entirely satisfactory for ordinary quantitative weighing.

This method, although apparently rather unconventional, deserves open-minded consideration by instructors of quantitative analysis, as it is somewhat quicker even than the two-swing system, offers the simplest device for putting the beam in vibration and, like magnetic damping, avoids all computations of center of swing. Not only is time and effort saved, but errors can be reduced in weighings of substances affected by contact with air.

[3] LIN, "An evaluation of the methods of using analytical balance," J. CHEM. EDUC., **16**, 340–3 (1939).

[4] BOOTH AND DAMERELL, "Quantitative analysis," McGraw-Hill Book Co., Inc., New York City, **1940**, pp. 22–3.

The New England Association of Chemistry Teachers[1]

RALPH K. CARLETON Rhode Island State College, Kingston, Rhode Island

TO THOSE whose association with the American Chemical Society has extended over some years, the name of Lyman Churchill Newell is synonymous with chemical history. Many are familiar with his activities in connection with the formation and development of the Division of Chemical Education and the Division of the History of Chemistry. But there is another organization with which Dr. Newell was intimately associated during his lifetime and to which he gave freely of his time and energy. That was the New England Association of Chemistry Teachers.

Although the records of this organization have been kept in a rather complete form during the period of its existence, like many another similar organization, it is difficult to state exactly when, where, and under what influences the New England Association of Chemistry Teachers came into being. By quoting from an article by the late Professor Newell,[2] a charter member and first president of the Association, an idea may be gained of the circumstances surrounding the origin of the group.

"Men of kindred tastes and aims have always sought inspiration in union. This principle is especially applicable to scientists. It is not unusual, therefore, that the New England Association of Chemistry Teachers should have come into existence through the desire of several teachers of chemistry to have an organization. Probably the first dynamic suggestion which led to the establishment of our Association was made jointly by Mr. Frank Rollins and Mr. John W. Hutchins. These two men were planning a chemical meeting of the Eastern Physics Teachers. The possibilities of such a single meeting were so marked that they decided to abandon the idea of a single meeting and agitated the project of an association to be devoted exclusively to chemistry."

Subsequent to the suggestions of the two men mentioned above, preliminary meetings were held for the purposes of informal discussions. At these meetings, Mr. Rollins, who at that time was the teacher of chemistry in the high school at Newton, Massachusetts, expounded his views on the teaching of chemistry with enthusiasm, and emphasized the necessity of having an organization which should inspire others to raise and maintain the standard of chemistry teaching. How well the Association has succeeded in doing just that will be discussed later. The outcome of these preliminary discussions was a formal meeting held on Saturday, February 19, 1898, at the high school, Malden, Massachusetts. On this day the New England Association of Chemistry Teachers was founded. A constitution was adopted and officers elected. Sixteen persons became charter members.

Professor Newell was chosen as the first president and served faithfully during his term of office. His influence had much to do with the interest in this new organization; he was a beloved companion of chemical educators, both those in the college field and those engaged in secondary-school work, a tower of strength to the new movement; his helpful interest and active participation remained unabated until his death in 1933. His wise counsel and sound advice were often sought by the younger members of the Association, and it was largely through his long service as Curator that the Association became the possessor of a number of valuable gifts.

It seems especially significant, if not a little amusing in these days when every organization strives to main-

[1] Presented before the Division of the History of Chemistry at the 98th meeting of the A.C.S., Boston, Massachusetts, Sept. 11–15, 1939.

[2] NEWELL, "History of the New England Association of Chemistry Teachers from the first to the fiftieth meeting," *Report N.E.A.C.T. Fiftieth Meeting*, April 25, 1914.

tain its membership, to observe that the original constitution of the Association limited the number of active members to fifty persons. The inadequacy of this number was soon realized, however, for in November, 1902, the limit was raised to seventy-five where it remained until February, 1914, when it was proposed that "the number of members, active, associate, and honorary shall be unlimited." Such is the case at the present time.

An important innovation attempted by the Association was the printing of the reports of its meetings, beginning in November, 1898, at the time of the third meeting. These reports, published continuously since that date, contain the papers presented at the meetings, together with a complete record of the proceedings of all the meetings of the Association. The reports appear four times during the year. From time to time, financial conditions permitting, papers which have not been previously presented at any meetings have been solicited from outstanding scientists, though this practice has been followed only to a limited degree. At the present time, it is possible for one to subscribe to the REPORT without holding membership in the Association.

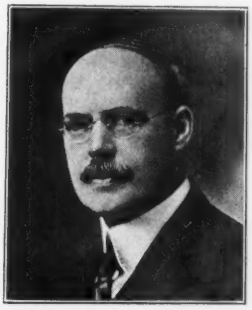
It was in 1902 that the organization inaugurated a system of excursions to industrial plants in Boston and vicinity. This valuable adjunct to the regular meetings of the Association has been continued without interruption to the present time and is always planned for in connection with the regular meetings throughout the year. The owners or directors of manufacturing firms throughout New England have always shown the utmost courtesy and willingness to coöperate with the Association in planning visits to their respective plants.

Steps were taken at the thirty-ninth meeting held at Boston University, December 22, 1910, toward the incorporation of the Association. At that meeting it was voted that the Executive Committee be instructed to proceed with the incorporation. In anticipation of gifts to the Association it was voted, further, to appoint a Curator of all gifts (except money) such as books, apparatus, specimens, and lantern slides. In addition Boston University was, at that time, to be the repository of such gifts. The office of Curator was made permanent and the late Professor Lyman C. Newell was elected the first incumbent. In this capacity he served faithfully until his death.

On January 6, 1911, the Association was incorporated under the laws of Massachusetts. In the articles of incorporation it states significantly that the incorporation is:

"for the purpose of promoting efficiency in the teaching of chemistry; for the purpose of making investigations in the science of chemistry and its allied subjects, and the dissemination of knowledge resulting therefrom; for the purpose of acquiring and holding apparatus, books and other property whether real or personal, incidental and necessary for carrying out the purposes aforesaid."

The incorporation of the Association was made in view of the fact that it was the recipient of gifts and yet was not legally entitled to receive them or transmit them, nor was there anyone legally empowered to act as the possessor of gifts. This latter became the function of the Curator.



PROFESSOR LYMAN CHURCHILL NEWELL, FIRST PRESIDENT OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

Toward the end of this same year, the suggestion was made to Mrs. Rufus Phillips Williams that the Association would like to honor the memory of the second president, Rufus Phillips Williams, who died August 23, 1911, by purchasing his books for the Association Library. Conferences with Mrs. Williams finally resulted in the gift of the Rufus Phillips Williams Memorial, consisting of rare old volumes on chemistry, as well as other valuable material collected by Mr. Williams during his long years of service as teacher of chemistry in the English High School, Boston, Massachusetts. These books and memorabilia were accepted by the Association February 3, 1912, and deposited in the Library of Boston University. Here they remained until 1935 when the books, still the property of the N.E.A.C.T., were removed to the Olin Library of Wesleyan University, Middletown, Connecticut.

Committee work early became important, largely because of the nature of the topics discussed, which needed further investigation. For example, in 1915, the following committees were functioning and reports from each were included in the Association reports of that year:

(*a*) *Committee on New Apparatus.*

This committee helped to keep the members of the Association in touch with many of the new developments in the way of new apparatus both for laboratory work and for industrial purposes as well.

(*b*) *Committee on Current Events.*

In looking over the report of this Committee for 1915, one finds an excellent means of ascertaining the vital problems confronting chemists of that day, *viz.*, such for example as (1) the possibility of the Germans producing artificial rubber from milkweed, (*cf.* studies by Thomas Edison), (2) the use of hydrogen for changing fatty waste into edible oils, (3) development of our

potash sources such as Trona Lake, etc., and many others.

A quotation from the REPORT of the year 1915[3] impresses one.

> "It is surely fitting that this Association should take notice of the first National Exposition of Chemical Industries held in America. The exposition was held in the Grand Central Palace in New York, and a report of the exposition is given in the *Scientific American* for October 2, 1915. Many teachers will want to read the entire report of this exposition. A quantity of new apparatus was displayed; several new methods for utilizing waste products were suggested. "Made in America" glass appeared in abundance. Black smoke issuing from a chimney was immediately dispelled by passing a current from a 100,000-volt transformer through wires arranged at the mouth of the chimney. The smoke was precipitated, not burned."

How far chemical science has progressed in a quarter of a century!

In recent years committees of the Association have studied various aspects of chemical education with significant results. The new chemistry syllabus of the College Entrance Examination Board[4] incorporates to a large extent the philosophy and the form of a syllabus[5] suggested by the N.E.A.C.T. More recently a very active committee has been considering the content of the "general chemistry course."

In the March 5, 1921, REPORT is found an interesting situation. Seventy members were present and at this meeting over 112 persons were elected to membership. This is probably the largest number ever elected at one time. At present there are over 350 members.

For the first time there appears a division of the organization into four sub-groups or as they have since been known, Divisions, through which the Association has functioned to date. The membership throughout New England was grouped into four sections or divisions, *viz:*

(*a*) *Northern Division,* including Maine, New Hampshire, and Vermont.
(*b*) *Central Division,* including eastern Massachusetts.
(*c*) *Southern Division,* including the entire state of Rhode Island and that portion of Massachusetts within easy reach of Providence.
(*d*) *Western Division,* including Connecticut and western Massachusetts.

For the past eighteen years these four divisions have operated interdependently and have enabled the parent organization to become one of the most valuable and effective science agencies in the country. Each division is responsible for two meetings within its own territory each year, at which time the respective chairmen plan interesting and instructive programs.

In the REPORT of the Ninetieth Meeting held at the Chapman Technical High School, New London, Connecticut, is presented a "Report of the First Annual Chemistry Contest Held at Rhode Island State College"[6] on May 10, 1924. The membership of the N.E.A.C.T. and especially that of the Southern Division has supported wholeheartedly the contests, which have become an annual event.

In 1936 appears the introduction of an amendment to the original constitution of the Association to cover the development of an Endowment Fund of the Association. The purpose in setting up this Fund was obvious in that it was to care for bequests of various sorts that were being directed to the organization. The funds were to be in the hands of a Board of three trustees, which was to have complete charge of the investment and disbursement of all income from such funds. A very important aspect of this step was the fact that the income from such funds was to be expended wholly or in part for improving and publishing the REPORTS. If any emergency or special need arises, all or any part of the current income may be used for that purpose, upon approval by the Board of Trustees. Most significant of all is the fact that "if and when the New England Association of Chemistry Teachers shall cease to exist, all moneys in the Endowment Fund shall be transferred to the Publications Trust Fund of the Northeastern Section of the American Chemical Society to help promote the publicational activities of that section."

The most recent development of the Association has been the inauguration of annual summer conferences. The first was held at the University of Vermont, August 16–19, 1939. The program centered around five distinct themes, each of vital interest to teachers of chemistry: (1) Introductory College Chemistry; (2) Assimilation of New Material; (3) Progressive Teaching; (4) Organizations; (5) Consumer Chemistry. The topics discussed were chosen with an idea of appeal to both college and secondary-school teachers. A second conference at the University of Maine, Orono, Maine, August 13–16, 1940, attended by over 200 members and guests, offered an equally ambitious program. The third conference is scheduled at the University of Connecticut during the week of August 10 this coming summer.

Through its papers, discussions, and especially its many and various committees, reports, etc., the Association has attempted to be a distinct help to those whose business it is to present the subject of chemistry to others, and to knit them together with a common bond for a common purpose. To advance the profession of teaching chemistry in New England, to help clarify and codify where such aid is needed, and to foster coöperation with all chemists, have been constant aims. Consequently, each of the four divisions has always tried to appreciate having a part in the parent organization's work, and to deserve the confidence and coöperation the Association's officers have so generously extended to it, while at the same time maintaining and developing its own divisional individuality and becoming a worthy branch of a worthy parent vine.

[3] "Report of Committee on Current Events," *Report, N.E.A.-C.T. Fifty-Fourth Regular Meeting,* December 11, 1915, pp. 6–8.
[4] J. CHEM. EDUC., **17,** 443 (1940).
[5] J. CHEM. EDUC., **16,** 46 (1939).
[6] *Cf.* CARLETON AND INCE, "Lessons from twelve years of chemistry contests," J. CHEM. EDUC., **13,** 464–8 (1936).

An Excerpt from Lavoisier's Laboratory Journal

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NONE of Lavoisier's studies has been more publicized than his cyclic analysis and synthesis of air. This clever use of mercury and mercuric oxide has come to be known as "Lavoisier's Experiment *par excellence*." "This is the most complete proof that can be accomplished in chemistry," declared he, and the justness of this appraisal is manifested by the regularity with which this experiment is held up as a model. Even the beginners in chemistry are made familiar with this masterly cross-examination of Nature. Long after they have forgotten the details of the experiment or its objective, many chemists retain a mental picture of the apparatus: the furnace and the retort with its curved neck extending into a bell jar (Figure 1).

The printed accounts of this study[1] are records of experiments for which the original notes are no longer preserved, or, more likely, these accounts are compiled from combinations of several trials, for Lavoisier admitted that "it is difficult in one experiment both to preserve the whole air upon which we operate and to collect the whole of the red particles, or calx of mercury, which is formed during the calcination." Neither the formation nor decomposition of mercury oxide were original with Lavoisier; his merit consisted in combining them.

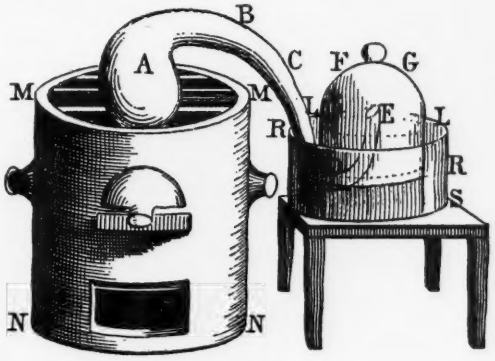
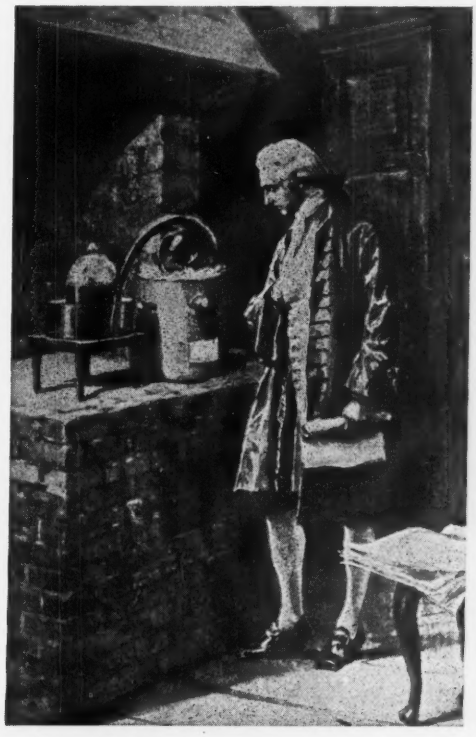


FIGURE 1

The entries in his laboratory journal referring to this experiment patently correspond to his first attempt. The account is not complete, the work is exploratory, some of the measurements are on a loose sheet between the pages of the notebook, a half page was left blank for future entries that were never made.

The experiment was carried out in April, 1776, and the memoranda are set down in Volume IV of his laboratory journals, preserved in Paris in the archives of the Académie des Sciences. Berthelot, in his abstract of these notebooks, states that this volume was less regularly kept than its forerunners,[2] and Lavoisier's own



From French, "The Drama of Chemistry." Courtesy of The University Society, New York.

THE EXPERIMENT *par excellence* (FROM A PAINTING BY THURE DE THULSTRUP, 1848–1930)

record states that he was obliged to interrupt this experiment because of a change of residence (to the Arsenal). Despite the fragmentary character of these notes, they have great sentimental, if not historic, interest because they are apparently the only remaining original record of the most famous of his experiments. This fact justifies the publication of notes that were never intended for the public eye. Furthermore, a glimpse behind the scenes is usually alluring, often enlightening, and sometimes disillusioning.

A glance at Lavoisier's sketches demonstrates why he did not make the plates for his *Traité*, a task that was admirably accomplished by Madame Lavoisier. His handwriting is not easy to read, and considerable study

[1] *Memoires de l'Academie des sciences, année 1777*, 185 (1780), reproduced in "Oeuvres de Lavoisier," Vol. 2, **1862**, p. 174; LAVOISIER, "Traité élémentaire de chimie," **1789**, p. 35, reproduced in "Oeuvres," Vol. 1, **1864**, p. 36.

[2] BERTHELOT, "La revolution chimique," Paris, **1890**, p. 269.

is required to decipher some of the words; a reading glass is a great aid. Though he used modern French

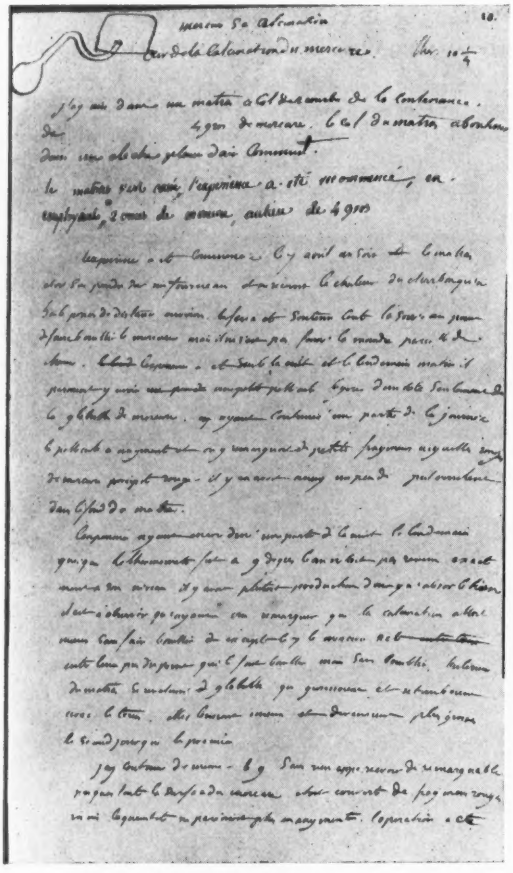


FIGURE 2

mercure sa calcination
air de la calcination du mercure
j'ay mis dans un matras a col du courbe de la contenance de 4 gros de mercure. le col du matras aboutissoit dans une cloche plein dair commun.
le matras s'est cassé, l'experience a eté recommencé, en employant, 2 onces de mercure, aulieu de 4 gros l'experience a eté commencé le 7 avril au soir—le matras etoit suspendu sur un fourneau et ne recevoit la chaleur du charbon qu'a 5 a 6 pouces de distance environ. le feu a eté soutenu cont. le soir au pouvoir de faire bouillir le mercure mais il ne s'est pas formé le moindre parcelle de chaux. l'experience a eté suit la nuit et le lendemain matin il parrasoit y avoir une petite pellicule legere d'un cote seulement de la globule de mercure. ayant continué une partie de la journée la pellicule a augment et on y remarquoit de petits fragmens aiguilles rouges de mercure precipite rouge.—il y en avoit aussy un peu de pulverulent dans le fond du matras. . . .

in his printed works, these notes contain many early forms and archaic spellings. Since more detailed and polished presentations are available, only a portion of the record will be given here, with a hope that these samples may serve as a guide to those students who may wish to test their linguistic skill by reading the only known private account of Lavoisier's great experiment.

On the pages between those reproduced here Lavoisier records that on the morning of the 10th, the absorption seemed to have ceased, 48 hours later more calx appeared, after 80–100 hours its quantity was rather considerable. At this point he stopped the heating because of the move into his new residence. He found the residual air extinguished a flame but gave with nitrous air (nitric oxide) a little red vapor, six volumes of the air and one volume of oxide shrank to $5^7/_8$. The residual air mixed with dephlogisticated air (oxygen), which he knew to be not more than fifty per cent pure, was tested with a flame; 8:1 extinguished, 5:1 supported the flame about as well as ordinary air. Two volumes of this mixture with one volume of nitrous air shrank to $1^5/_8$; three volumes plus one volume gave $3^1/_4$, but even this mixture contained an excess of nitrous air because the addition of a little common air produced red fumes. The air from the calcination gave no precipitate with lime water. These items show how uncertain he was at the time of this first study in contrast to the assuredness he exhibited in his later reports. The story of the evolution of his antiphlogistic ideas has been told too often to need repetition here.

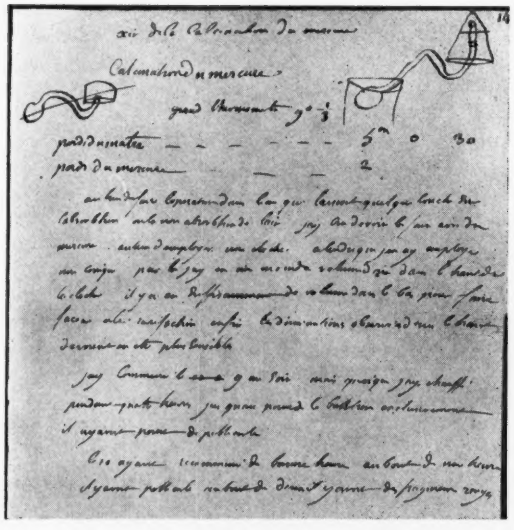


FIGURE 3

. . . . au lieu de faire l'operation dans l'eau qui laissoit quelque couche sur l'absorbtion ou la non absorbtion de l'air j'ay cru devoir le faire avec du mercure. au lieu d employer une cloche cylindrique jen ay employe une conique par la j'ay eu un moindre volume d'air dans l haut de la cloche . . . .

The Preparation of Weston Standard Cells

WARREN C. VOSBURGH and PAUL F. DERR
Duke University, Durham, North Carolina

IT HAS been the experience of one of the authors that the Weston standard cell is one of the easiest of cells to reproduce. While the preparation of cells of the highest degree of reproducibility and constancy requires experience and much care,[1] most chemists should be able to make cells suitable for standards when the highest degree of precision is not required. To test this opinion, a set of directions was written and was followed carefully by several students who kindly coöperated in the test. With one exception the students were either seniors or graduate students. None had had previous experience in making Weston cells.

The chemicals used were of the best commercial grade, with no further purification, except that the mercury had been redistilled and the mercurous sulfate was specially prepared by the method given.

DIRECTIONS FOR THE PREPARATION OF WESTON CELLS

Vessels.—It is assumed in the directions following that glass vessels of the H-type will be used, with sealed-in platinum (or tungsten) wires for connection to the two electrodes. The quantities of the materials specified are estimated for vessels made of 12- to 15-mm. (inside diameter) glass tubing and 15 to 18 cm. high and about 5 cm. wide. For vessels appreciably larger, the quantities would need to be increased. The tops of the vessels may be closed by rubber stoppers, or sealed in a flame if desired. The vessels should have platinum (or tungsten) wires sealed in near the bottoms of the legs of the vessel; for convenience and for protection of these wires it is well that copper wires of fairly small diameter be fastened to the sealed-in wires and tied securely to the glass vessel. The copper wires may be soldered to the platinum wires. If the vessels are of pyrex glass and the sealed-in wires of tungsten, the outer ends of the tungsten wires may be covered with brass by heating in an oxygen-gas flame with a piece of brass brazing rod, with borax as a flux. The copper wire can then be soldered to the brass.

Mercurous Sulfate.—Dissolve about 10 g. of finely ground crystals of mercurous nitrate in a solution prepared by the dilution of 6 ml. of concentrated nitric acid to 100 ml. When the crystals are completely dissolved, dilute to 200 ml. Filter through asbestos or glass wool if the solution is not clear, or if any material remains undissolved. Add the mercurous nitrate solution drop by drop with vigorous stirring to 200 ml. of 2 *M* sulfuric acid solution. The latter may be prepared by the addition of 35 ml. of concentrated acid to 300 ml. of water, a third of the resulting solution being diluted with an equal volume of water and retained for use as a wash solution. Wash the mercurous sulfate precipitate (which should be pure white in color) by decantation with five 15-ml. portions of the 1 *M* sulfuric acid wash solution and then add the remaining 1 *M* acid solution and allow the precipitate to digest at room temperature in the dark overnight or longer.[2]

Cadmium Sulfate Solution.—Prepare 60 ml. of either 0.015 *M* sulfuric acid solution or 0.1 *M* acetic acid solution, the concentration correct within 10 per cent. To this solution add about 70 g. of finely ground cadmium sulfate crystals (3 $CdSO_4 \cdot 8H_2O$) and stir *vigorously* (by means of a mechanical stirrer) for at least 30 minutes. Filter this solution, preferably through asbestos or pyrex glass wool, if any foreign matter is present in suspension. Suspended cadmium sulfate is not objectionable.

Cadmium.—Heat one end of a stick of cadmium in a burner flame until the metal melts and falls in drops. The drops should be allowed to fall on a watch glass or other clean surface where the metal solidifies to form a thin disc that can be easily cut into pieces of any desired size.

Preparation of Cells.—Clean the cell vessel thoroughly and dry it. Weigh the vessel to the nearest tenth of a gram. Introduce into one leg of the vessel enough mercury to cover the sealed-in wire completely and weigh again. A quantity of cadmium equal to between 10 and 12 per cent of the mercury is to be added next to make cadmium amalgam. Weigh the required amount of cadmium to the nearest tenth of a gram and add it to the mercury in the vessel. Cover the cadmium and mercury to a depth of one to two inches with approximately 0.01 *M* sulfuric acid solution. Immerse the amalgam leg of the vessel in warm water, heat the water, and shake the vessel until the cadmium is completely dissolved and the amalgam is of uniform composition. Allow the amalgam to cool, and remove the acid solution by means of a pipet to which a rubber tube is attached, so that the pipet can be operated while watching the lower end. Rinse the amalgam once with a small portion of saturated cadmium sulfate solution, then cover it to a depth of two centimeters with the saturated cadmium sulfate solution. Grind some selected cadmium sulfate crystals, and drop the finely ground crystals into the solution until the amalgam is covered to a depth of about one centimeter. Then add coarser crystals up to the level of the cross arm. If some of the solution runs over into the other arm it will do no harm.

[1] WOLFF AND WATERS, "Clark and Weston standard cells," *Bur. Standards Bull.*, **4**, 1–80 (Dec., 1907); VOSBURGH, "Conditions affecting the reproducibility and constancy of Weston standard cells," *J. Am. Chem. Soc.*, **47**, 1255–67 (May, 1925).

[2] For cells of the highest quality it is desirable that the mercurous sulfate be digested under the acid solution, together with a little mercury, at a temperature near the boiling point for several hours.

Add enough mercury to the empty leg of the tube to cover the sealed-in wire, and then enough cadmium sulfate solution to cover the mercury to a depth of about two centimeters. Separate the mercurous sulfate from the acid solution (under which it has been kept) by filtration in a Gooch crucible with a small disc of filter paper covering the bottom. To rinse the mercurous sulfate from a beaker or flask, a 0.01 *M* (or more concentrated) sulfuric acid solution may be used, *but not water*. Wash three times on the filter with 5-ml. portions of the cadmium sulfate solution. Avoid exposure of the mercurous sulfate to air any longer than necessary after washing. Transfer the mercurous sulfate from the crucible to a small beaker, add 10 ml. of cadmium sulfate solution and about 2 g. of finely ground cadmium sulfate.[3] Mix thoroughly, allow to settle, and decant the solution. Wash with two more 5-ml. portions of cadmium sulfate solution, add 5 ml. more, and then by means of a glass tube narrowed at one end transfer some of the mercurous sulfate paste to the mercury side of the cell vessel, allowing it to fall through the solution above the mercury and come to rest on top of it. Enough of the paste should be added to give a layer about one centimeter deep when it has settled. Do not allow mercurous sulfate to get into the amalgam side of the vessel. Add finely ground cadmium sulfate crystals until a layer about one centimeter deep has been formed above the mercurous sulfate, then add coarse crystals up to the cross arm of the vessel. Add cadmium sulfate solution until the level of the solution is above the cross arm. Stopper the vessel. The cell may be expected to come to equilibrium within 0.1 mv. in about a week and within 0.03 mv. in about a month.[4]

RESULTS

After preparation, the cells were placed in an oil bath at 25° and measured frequently by the authors by means of a Leeds and Northrup Type K potentiometer and a group of standards probably reliable to 0.01 mv.

It is of interest to compare the cells of this investigation with similar cells constructed by experienced workers with more highly purified materials. For electrolytes 0.01 molar with respect to sulfuric acid (saturating a 0.015 *M* acid solution with cadmium sulfate dilutes the acid to 0.011 *M*), the usual value at equilibrium is 1.01805 v. and under the best conditions deviations should not be more than 0.01 mv. For cells with electrolytes 0.07 molar with respect to acetic acid, the value is 1.01802 or 1.01803 v.; this is a little less certain than the other because fewer cells of this type have been made.[5]

The largest deviation from the correct value within one day of preparation was 0.67 mv. or about 0.07 per cent, while the average deviation for the twenty cells was ±0.15 mv., or less than 0.02 per cent. A week later the maximum deviation was 0.2 mv., or 0.02 per cent, and the average deviation ± 0.06 mv., or appreciably less than 0.01 per cent. Some time after the preparation of eight of the cells it was discovered that by mistake the mercurous sulfate used in them had been prepared by precipitation from a solution containing too little sulfuric acid. Some of the cells made with the inferior mercurous sulfate attained values lower than the normal, but did not vary greatly. Ten of the twelve cells made with good mercurous sulfate had an average deviation of less than 0.03 mv. (0.003 per cent) after two months. The average electromotive force of eight of these cells made with acetic acid was 1.01802 v. and that of two cells made with sulfuric acid was 1.01806 v. If the students coöperating in this test may be considered typical of inexperienced workers, it may be concluded that relatively inexperienced technicians should be able to construct saturated Weston cells giving an electromotive force at equilibrium within a few hundredths of a per cent of the correct value.

It should be mentioned that these cells are *saturated* Weston cells and differ from the unsaturated standard cells available from commercial sources in having a larger temperature coefficient. A change of temperature from 20° to 30° C. causes a change of 0.49 mv. or 0.05 per cent in the electromotive force. An approximate temperature correction may be made by means of the formula

$$E_t = E_{25} - 0.000046\,(t - 25)$$

in which t is the Centigrade temperature. This formula should hold within 0.003 per cent between 18° and 30° and within 0.01 per cent between 15° and 35°. For a more precise correction, Wolff's temperature formula[6] should be used.

A modified Weston cell has been described[7] that has a temperature coefficient between a quarter and a third that of the ordinary saturated cell. The modified cell is a little more difficult to make than the ordinary cell, but with proper precautions it is possible to reproduce it

[3] The amount of cadmium sulfate to be added to the mercurous sulfate should be from one-quarter to one-half of the amount of the latter, estimated roughly by volume.

[4] By careful exclusion of oxygen and evacuation to insure removal of oxygen from the amalgam, cells have been made to come to equilibrium within 0.01 mv. immediately. See ref. 7 below.

[5] Two cells containing this concentration of acetic acid have been observed for a period of over nine years. These cells and others made subsequently have been as satisfactory with respect to constancy as cells containing 0.01 *M* sulfuric acid. In one respect they may prove to be superior. So far, no reaction of acetic acid of this concentration with the cadmium of the amalgam to give hydrogen has been observed. Occasionally, however, cells containing sulfuric acid are spoiled by the generation of hydrogen at the amalgam, though most of them show no signs of such action over periods of many years. It seems probable that this reaction is catalyzed by certain impurities. When impurities may be present and when long life is of more importance than high precision, acetic acid is probably the better choice of the two acids.

[6] WOLFF, "The temperature formula of the Weston standard cell," *Bur. Standards Bull.*, **5**, 309–37 (Sept., 1908); VOSBURGH, "The applicability of Wolff's temperature formula for the Weston standard cell," *J. Optical Soc. Am. and Rev. Sci. Instruments*, **12**, 511–517 (May, 1926).

[7] VOSBURGH, GUAGENTY, AND CLAYTON, "Saturated standard cells with small temperature coefficients. II," *J. Am. Chem. Soc.*, **59**, 1256–8 (July, 1937).

about as well. To the cadmium amalgam is added 10 to 15 parts of bismuth for every 100 parts of 10 to 12 per cent cadmium amalgam.[8] Also, the electrolyte of the modified cell is saturated with the double salt of cadmium and sodium sulfates, $CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$ as well as with hydrated cadmium sulfate.[9] Wherever solid cadmium sulfate is placed in the ordinary Weston cell, a mixture of cadmium sulfate and the double salt must be substituted in the modified cell. Cells of this type have shown excellent constancy for over three years and there is no reason to expect any greater number of failures than with the Weston cell.

[8] VOSBURGH AND PARKS, *J. Am. Chem. Soc.*, **61**, 652–4 (1939). The bismuth will amalgamate readily on heating if a small current is passed between the amalgam and the dilute acid solution above it, with the amalgam as cathode.

[9] Solubility data for this system are to be found in "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, **1928**, Vol. IV, p. 340.

Fire Fighting—A Cog In the Wheel of National Defense

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A UNITED Press report from London, England, October 5, 1940, read: "Fifty men of the London Fire Brigade lost their lives fighting bomb-started fires last month, and 501 others were injured, some seriously."

An article appearing in *Life* entitled, "London Fire Fighter," portrayed the activities of 30,000 members of the Auxiliary Fire Service who augment London's regular fire brigade. The members of this service receive four pounds a week and their keep, and devote all of their time to fighting fires started from incendiary bombs dropped on London. Frequently these duties are performed while under fire from machine guns, bombs, etc., and the risks are made especially dangerous because the location of the men is apparent from the light of the fires that they are fighting. Therefore, they are ready targets for aerial attacks. Daily press reports reveal that fighting fires in modern warfare is one of the most important defense activities. It is also significant that three men from New York City's Fire Department were recently sent to England to study fire-fighting activities there.

During the past year, the author has developed a chemistry course in the Division of Public Service Training for students preparing for the fire department in the city of New York. Since it has been apparent that fire is a modern weapon of warfare, the Department of Chemistry at the School of Business and Civic Administration has placed special emphasis on the fact that extinguishing a fire can be thought of as reversing or slowing down the reaction taking place in the combustion.

All the methods for altering the speed of a chemical reaction apply to the reverse reaction as well as the forward reaction, hence it seems logical to teach fire fighting along these lines. Fire extinguishing involves, therefore, slowing the reaction by cooling or by decreasing the concentration of reacting materials, or both, which in turn involves nothing different from the same means of slowing any other chemical reaction. It is only necessary to slow the reaction down to the point where the heat liberated by the reaction is produced at a slower rate than heat is lost to the environment; then the fire dies a natural death.

This approach has been adopted by the author in teaching fire extinguishing to the students preparing in the Division of Public Service Training for fire department service. The students have previously learned the means of altering the rate of a chemical reaction, and this approach has stimulated exceptionally lively discussions, as well as a better understanding of the methods of fire fighting.

The author feels that he is not presumptuous in taking this opportunity to call the attention of all teachers of chemistry throughout the United States to their obligation to teach to every student of chemistry the fundamentals of fire fighting, since this new weapon of defense is of prime importance in modern warfare. It seems obvious that in modern defense warfare every citizen must be alert to the danger of fire and prepared to extinguish, often single-handed, small fires before they grow large. This is a cardinal rule in safety at all times, and becomes more so in present-day warfare.

Since the writer is meeting such success in fitting this type of work into the pattern of fundamental chemistry, it is further suggested that the task may be done without necessarily changing the courses already established in the various schools. A start in the right direction would be to use the reaction of combustion for illustrating the application of the means of altering the reaction rate. From the author's experience, it is predicted that if this approach is taken, the teacher will find that the students are anxious to continue this type of thought beyond the mere introduction of the idea; the teacher will find good reason to expand upon this topic as the individual circumstances permit.

Since we are preparing for defense, we owe it to our country to teach every student passing through our hands more about fire extinguishing than is customary, so that this horrible weapon "fire" can be combated successfully. It is inevitable that, should this country be forced to defend itself from attack, every able-bodied citizen who knows something of fire fighting will be so much more of an asset. Chemistry students are the best fitted to learn fire fighting, and the author urges all his colleagues to accept the challenge before us.

The Qualitative Analysis of the Alkali Metal Group[1]

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THE qualitative analysis schemes used up to the present[2] for the analysis of the alkali, or soluble group have, in general, employed the procedure of baking the filtrate from the group immediately preceding. The baking procedure has two chief disadvantages, (1) the time required, and (2) the fact that, in the hands of inexperienced analysts, the baking is likely to be insufficient. In an effort to overcome these difficulties a simple modification of the procedure was tried. It consists essentially in separating the solution to be tested into two portions and then removing the NH_4^+ from one portion by means of the addition of NaOH and boiling. The resulting solution, which is free from NH_4^+, can be tested for the K^+ by the addition of acetic acid until acid and then the addition of a solution of sodium cobaltinitrite. The other portion can be tested for the Na^+. This general procedure has been applied by sophomore qualitative analysis students on a semimicro scale, and by freshmen qualitative analysis students on the macro scale.

Semimicro Scale.—The following are essentially the instructions used by a random group of students in a second year qualitative analysis course in which Vosburgh's[3] text is used. The procedure assumes that group precipitations of the HCl, H_2S, $(NH_4)_2S$, and $(NH_4)_2CO_3$ groups have been carried out, and that no PO_4^{-3} or $C_2O_4^{-2}$ are present. Other common negative ions do not interfere.[4] The test for NH_4^+ must be made on a sample of the original unknown.

SEMIMICRO SCALE

Procedure for the Na^+ and K^+ Tests

Evaporate the filtrate from the carbonate group in a 50-ml. beaker to a volume of approximately 3 ml. (This volume may be estimated by taking the clean beaker and pouring into it 3 ml. of water.) Remove one half of the solution (approximately 1.5 ml.) and save it for the Na^+ test.

Potassium Test.—Add 3 ml. of 6 *M* NaOH to the 1.5 ml. of the $(NH_4)_2CO_3$ group filtrate remaining in the 50-ml. beaker, and boil the resulting solution, while stirring, until the volume is approximately one ml. Add 2 ml. of water drop by drop, being sure to dissolve the deposited salts on the wall of the beaker. Now add 10 drops of 6 *M* NaOH. Boil slowly and test the vapors with a piece of moist red litmus. If the test for NH_3 is positive after evaporating to a volume of about one ml., repeat the NaOH treatment (10 drops) until no test for NH_3 is obtained. With the final volume of approximately one ml. add, with stirring, 6 *M* CH_3COOH, one drop at a time, until the resulting solution is slightly acid. (Some solid may remain undissolved, but this is not objectionable.) Withdraw approximately one ml. of the solution and centrifuge. Draw off 8 drops of clear liquid and add to this 20 drops of a solution of sodium cobaltinitite. (The $Na_3Co(NO_2)_6$ solution is prepared by adding 2 ml. of H_2O to one g. of $Na_3Co(NO_2)_6$ and stirring until dissolved.) Stir the solution vigorously and scratch the walls of the tube with a stirring rod. A yellow precipitate of $K_2NaCo(NO_2)_6$ shows the presence of K^+.

Sodium Test.—If K^+ was found add 5 drops of 6 *M* $HClO_4$; if a precipitate appears, centrifuge the mixture. (Filtration may, of course, be substituted for centrifugation.) Now add one drop of $HClO_4$ to the solution which stands above the precipitate in the centrifuge tube. If no further precipitation occurs remove eight drops of the clear liquid and proceed with the sodium test as indicated below. If, however, more precipitate does form, continue the $HClO_4$ treatment until no further precipitation occurs. This procedure is necessary because large amounts of K^+ will interfere with the Na^+ test. If K^+ was not present in the unknown the $HClO_4$ treatment is unnecessary.

Place 8 drops of the clear solution to be tested in a centrifuge tube and add 2 drops of 6 *M* CH_3COOH. Add to the resulting solution 20 drops of zinc uranyl acetate (sodium reagent). If no precipitate is formed scratch the inside of the tube with a stirring rod. If a quick-settling, greenish yellow precipitate forms and settles to the bottom of the tube the presence of the sodium ion is shown.

Macro Scale.—The following are essentially the instructions used by a number of students in a freshman qualitative analysis laboratory in which a modification of Cornog's[4] text was used. The PO_4^{-3} and $C_2O_4^{-2}$ were excluded from the samples of unknowns. The tests, as described, give excellent results on NH_4^+, K^+, and Na^+ content as low as five per cent.

MACRO SCALE

Procedure for NH_4^+, K^+, and Na^+

Preparation of the Test Solution.—Place one g. of finely powdered original unknown in a 100-ml. beaker and add 10 ml. of water. Boil the mixture for one minute with stirring. Filter and reject any precipitate. Divide the solution into two equal parts. Use one portion for the sodium test and the other for the ammonium and potassium tests.

Ammonium Test.—To the solution for the ammonium and potassium tests in a 100-ml. beaker add 2 ml. of 6 *M* NaOH and 6 ml. of 1.5 *M* Na_2CO_3. Cover with a watch glass and insert a piece of moist red litmus paper between the rim of the beaker and the watch glass. Heat the solution to boiling and observe the litmus paper.[5]

If the litmus paper turns *uniformly* blue, ammonium ion is present in the unknown. Filter and reject any precipitate and continue boiling the filtrate until the vapors coming off no longer

[1] Presented before the Division of Chemical Education at the 99th meeting of the A. C. S., Cincinnati, Ohio, April 10, 1940.

[2] NOYES AND BRAY, "A system of qualitative analysis for the rare elements," The Macmillan Co., New York City, **1927**, pp. 245–67, 466–86.

[3] VOSBURGH, "Introductory qualitative analysis," revised ed., The Macmillan Co., New York City, **1938**, p. 217.

[4] CORNOG, "The Iowa system of qualitative chemical analysis," 4th ed., The Clio Press, Iowa City, **1937**, p. 66.

[5] If a blue color appears only in spots it is probably due to spattering of NaOH.

show the presence of NH_3. Now add 0.5 ml. of 6 *M* NaOH and boil until no more ammonia comes off. Repeat the addition of NaOH and boiling until no NH_3 appears on first boiling the solution. Proceed to the test for potassium ion.

Potassium Test.—Acidify the clear solution from the ammonium test by adding, with stirring, 6 *M* CH_3COOH. To one ml. of this solution add 2 ml. of freshly prepared sodium cobaltinitrite made from 0.5 g. of solid sodium cobaltinitrite in 2 ml. of water. An immediate yellow crystalline precipitate of $K_2NaCo(NO_2)_6$ indicates the presence of potassium.

Sodium Test.—If the solution reserved for this test is highly colored add 3 ml. of 3 *M* $(NH_4)_2CO_3$ and filter off any precipitate. (If the reserved solution is colorless the $(NH_4)_2CO_3$ treatment may be omitted.) Add to the solution one ml. of 6 *M* $HClO_4$ and one ml. of 6 *M* HCl. If a precipitate is formed filter and reject it, and if potassium is present add more $HClO_4$ (one-ml. portions) until no more precipitate appears. If no potassium was found in the potassium test, the addition of $HClO_4$ is unnecessary. Test the solution with litmus paper, and if not acid, acidify with 6 *M* CH_3COOH. To one ml. of the solution add 3 ml. of sodium reagent (zinc uranyl acetate). The formation of a heavy, quickly settling precipitate indicates the presence of sodium. If no precipitate appears, shake for a moment before concluding that sodium is absent.

NOTES ON THE MACRO SCALE PROCEDURE

1. Ammonium ion gives the same test as the potassium ion, and must therefore be removed before testing for potassium. This is accomplished by addition of large quantities of OH^- ion, in the form of NaOH, and boiling off the ammonia that is formed. In addition to furnishing the necessary OH^- ion, the NaOH and Na_2CO_3 cause the precipitation of many cations as hydroxides or carbonates. Some of these might interfere with the potassium test if not removed.

2. The sodium reagent is intended to give a precipitate with sodium ions only, but if there is much K^+ in the solution, it will also be precipitated by the sodium reagent. $HClO_4$ will precipitate the greater part of K^+ ions, so that there is no longer enough to interfere with the sodium test. The purpose of the HCl is to remove any large amount of Hg_2^{+2} or Ag^+ that may be present, as these also may interfere.

The procedures presented here have several advantages over those generally in use. They are as follows.

1. Less time is required for the inexperienced student analyst to make the necessary tests.

2. The procedure can be used more successfully, as has been shown by at least a ten per cent margin in its favor.

3. The pedagogical value of the chemistry involved is at least as great, and is probably greater than that involved in the usual procedure.

4. The use of possibly explosive mixtures, such as alcohol in significant concentrations and perchloric acid, is avoided.

The author is indebted to Mr. Randall Bortner for his help in running several preliminary tests on the semimicro procedure.

An Electrically Heated Funnel Heater for Small Conical Funnels

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Contribution No. 6 of the Destilería Serralles, Mercedita, Puerto Rico

IT occasionally becomes necessary to conduct a hot filtration on a rather small scale. The common gas-heated, hot water jacket funnel heaters are convenient only for use with large funnels about 5 or 6 inches in diameter. Electrically heated funnel heaters, adaptable for use with small funnels of 4 inches diameter or less, are commercially available but are rather too expensive to make them a worth-while purchase for occasional use only.

The Cenco No. 16512 heating unit replacement for a Hotcone flask heater is inexpensive and can readily be converted into an excellent heater for small funnels. A hole, large enough to take the stem of a 4-inch funnel, is cut through the bottom of the cement and magnesia insulation surrounding the heating element, and through the asbestos disc beneath. The refractory cement surface in which the resistance is imbedded and the exposed magnesia in the drilled hole and on the bottom of the heating element are well saturated with a solution of sodium silicate (water glass). The heating unit is now heated in an oven at 105°C. or more, until the silicate has dried out. This serves to strengthen the surface, especially the drilled hole, and prevents chipping and crumbling of the refractory materials. The asbestos disc is sealed to the bottom of the heating element with more sodium silicate solution.

The heater is now fastened firmly to a 4-inch ring-stand ring by any convenient method, and the lead wires (suitably insulated) are connected to a rheostat. Conical funnels of 1- to 4-inch diameter can now be conveniently heated to any desired temperature. For use with the smaller funnels of 1- to 2-inch diameter, sets of rings such as are used on water baths are placed on top of the device to hold the sides of the funnel and permit more even heating.

[1] Present address: American Cyanamid Company, Stamford, Connecticut.

High-School Chemistry

Elements and Safeguards of Scientific Thinking[1]

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THE TEACHER of chemistry has an excellent opportunity, as well as a duty, to train pupils directly to think in the field of science. Teachers have believed that science was an organized body of subject matter which, if taught, would result in the application and use of the scientific method by pupils in their daily living. John Dewey has pointed out that science is as much a method of thinking as it is organized subject matter.

Eckels (*1*) has said, "Too many teachers assume that exposure to a body of subject matter which has its foundation in clear thinking automatically induces that process which led to its being." Recent surveys of business offices, coupled with the opinion of men like Nicholas Murray Butler, have shown that pupils are graduating from our high schools unable to think and formulate seasoned judgments. Strauss (*3*) has further shown that the pupil gains more in the tenth grade in his ability to think scientifically. As he proceeds on through high school and college, he actually loses his power critically to evaluate forked-road situations presented to him. He may be learning to think in specific subject matter areas, but he is unable to transfer the scientific method and use it in other situations.

Dashiell (*2*) has indicated that, "Transfer of training may take place in some situations but not in others. Transfer lies not in subject, student's general memory power, or attention or reasoning in general, but resides in those habits of responding in this or that way to that aspect or detail which is common to both situations." Transfer probably takes place when the pupil has isolated a concept from its surrounding material and uses it when he sees that a detail in the new situation is common with one in the old situation. If the pupil is loaded with subject matter so that he has no time to reason, and if he is not taught directly so to do, he will only memorize and selectively recall what he has learned.

A student who possesses meager, limited concepts associated with concrete previous experiences will not properly recall such experiences. Adequate concepts freed from elements associated with them produce free and versatile thinking, such as the following:

OBSERVATION OF METAL FOILS[2]

I'd like to tell you about some observations I made over the weekend. I was in the basement idling away my time, and I ran across some lead. I had a melting pot and put some of the lead in it and melted it. This led me to think about the melting of different metals. (*Association with element in past experience.*) As the foil off different objects interests me (*interest element and pleasurable experience of eating candy bars*), I obtained two different-looking foils. (*Purposeful observation.*) I took the fullest and heaviest small piece and melted it. It formed a substance like that which was formed on the melted lead, lead oxide or sulfide, I suppose. (*Past experience—correct concepts.*) Next I took a lot of this foil and alas, it melted into a metal, lead, just as did the other. (*Cautious repetition of observations—controlled experimentation—seeing elements in common.*) I had heard of lead foil and tin foil; these foils seemed amazing, they were so thin. I wanted to find tin foil and how different it was from lead foil. (*Spirit of discovery thoroughly awakened.*) This other foil I had was put into the pot and heated. The former was heated on a gas stove burner. This foil was bright and the heat had no effect on it. I heated it longer; still nothing happened. I thought tin had a lower melting point than lead, but I checked myself to make sure. (*Looked in books.*)

That eliminated tin. I looked in the table and saw that it must be aluminum which I had not thought about, and it had a much higher melting point. (*A second tentative hypothesis.*)

As I had an oxy-acetylene torch at my disposal, I heated the pot with this and obtained the desired temperature. (*Controlled experimentation—allowing but one variable.*) First I took a piece of sheet aluminum and melted it, and then I took the foil. Sure enough, they were the same. Well, after an interesting time, I can now tell the difference between lead and aluminum foil. However, I couldn't find a piece of tin foil, but I shall do some experimenting with it. Could the substances formed on those molten metals of lead and aluminum be lead and aluminum oxide, respectively? (*Additional problem.*)

In recalling past experiences the wide range of this student's experience was brought out. He certainly verified his inference or "hunch" about the aluminum foil experimentally, and he permitted only one variable, the increased heat of the oxy-acetylene torch.

An experiment some five months before had preceded the boy's work on foils. This experiment involved heating and noting the weight changes of samples of magnesium, zinc, and lead. The increase in weight due to the formation of oxides was observed, except in the case of the lead. The lead showed no gain in weight, but the boy noticed that yellow sulfur had gathered on the sides of the crucible. He deduced that as fast as oxygen was taken on sulfur was given off; therefore, the sulfur was an impurity. Exceptions were given special attention in the case. In

[1] Presented before the Division of Chemical Education at the 100th meeting of the A. C. S., Detroit, Michigan, September 10, 1940.

Critical evaluation made by Dr. Rufus Reed and Dr. Catherine Cassidy, and Workshop Course, Western Reserve University, Cleveland, Ohio, Summer, 1940.

[2] By LEWIS SEYFRIED, Normandy High School, St. Louis, Missouri.

teaching for transfer of training, it is therefore well to present pairs of situations where one factor and an opposite are present. In this manner concepts are cleared.

Instructors can teach only what they know. It should be obvious that a teacher could not present the scientific method with safeguards in specifically organized pupil experiences unless he understood and used the scientific method himself. Chemistry teachers outside the laboratory too frequently become a prey to emotional appeals and prejudices of every sort. For this reason, the training of in-service teachers in the use of the scientific method is of primary importance.

A good teaching technic would be to present pairs of situations where one factor and an opposite would be present. The teacher might then define the element, indicate the class to which it belongs, and the characteristics which distinguish it from other elements to which it is similar. An example would be to test SO_2, CO_2, and CaO in distilled water with litmus. The action of any combination of metals in the electromotive series could be used and their reaction to HCl shown.

One caution, however, is that the teacher must be sure that the student has dissociated the concept from other elements occurring with it; otherwise hazy concepts occur, and any transfer to solving problems in new situations will be lost.

Failure on the part of the pupil to define a problem is due to several factors: the lack of adequate concepts; he has not the factors which will place the elements in a class clearly in mind; he lacks appropriate terminology to differentiate terms; illustrations, examples, or experimental activities were not presented in a forceful way; he has failed to set up evaluating criteria in his mind to check his results.

The failure to evaluate the competence of authorities studied, their technics and materials, whether the work has been checked or whether the authority has an "ax to grind," may lead to blocked knowledge. A boy brought a religious pamphlet to school, given him by his mother. The pamphlet indicated that the family would be poisoned if they ate food cooked in aluminum utensils. A class discussion soon brought out the fact that the man writing the pamphlet was not a competent authority.

In making a comparison, pupils will invariably cite facts which prove that two elements are in two separate classes. A comparison of CO and CO_2 would usually end in the pupil classifying the compounds as monoxide and dioxide. If the pupil's attention is directed first to identifying facts, and then to preparing a list of points of likeness as well as points of difference, he would see that they were related on the basis of the amount of oxygen present. With the concept freed, at a later date, he might think of applying his knowledge to the stoking of furnaces.

An investigation by one pupil was the result of observing that a silver chloride precipitate dissolved in an excess of sodium chloride. He performed a number of experiments to test the solubility of silver chloride. He was careful to run controls and allow only one variable. After a number of experiments which resulted in blocked knowledge, he consulted a book. He was not satisfied with what the book said, so he decided on a course of action of his own. Pupils even at the college level are too prone to put down what the book says, rather than propose several explanations for their observations. The boy observed the light of a conductivity apparatus stayed on when the electrodes were in a mass of silver chloride. One book said that silver chloride ionized when heated to the point of fusion, if carbon electrodes were used. The inference was that the silver chloride must ionize if it carried a current, but this high-school pupil wondered why the light in the circuit stayed on after the mass had cooled. He proposed several theories and verified one by amalgamating the silver with mercury. He drove the mercury off and found that a bridge of silver carried the current, the silver having been reduced by the action of carbon on silver chloride. He selected the most probable consequence and followed it up. He was not satisfied with what the book said. The plan of action was not the easiest nor the most common method for studying the solubility of silver chloride.

Certain errors are common to the inductive type of thinking. For example, a pupil may assume that all foils contain tin, because the expression "tin foil" is used. He might believe that assumption unless he checked it by testing candy bar wrappers. He might assume that all compounds ionize after testing a few inorganic compounds. His assumptions would be wrong because of a poor selection of experimental facts. He might make errors in observing wrong relationships. He might believe that the electron was as large as a small pea, just because a picture in a book had it drawn that way.

Sometimes appropriate or valid principles cannot be recalled. Again, the inference drawn may not be correct because more than one variable has been allowed during the process of experimentation. Other errors in drawing inferences may be: errors in premise, that is, assumed, supposed, or proved propositions; ambiguities or double meaning in language; errors in emphasis; errors in inclusion and distribution; errors due to form of inference methods; errors due to familiarity with subject matter; or mixing emotion and thought, resulting in grooved thinking and inflexibility. The human mind may escape reality and draw the wrong inferences by depending on authority instead of personal investigation; thinking that what exists is best; personifying impersonal forces (as thinking certain racial groups are responsible for misfortunes); attempting to influence thought by an appeal to character rather than point of issue; appeal to authority, to force, to sentiment, or attempt to throw the burden of proof on the challenger. This last is used by quacks, saying, "You do not know these influences do not exist."

Drawing inferences is one general way of thinking. A second method, as pointed out before, is to analyze situations and attempt to bring about a synthesis of

the important elements in order to solve problems.

Imperfect analyses usually result from failure to attend to essential elements or from focusing on the wrong elements, because of repression, suppression, or prejudice.

Pupils in studying for examinations frequently study what they think the teacher will ask for, instead of organizing their knowledge. The newer educational methods are moving away from emphasis on examinations and marks, and the criteria of evaluating pupil performance will probably be based in the future on the pupil's use of his knowledge in solving problems presented in extra-curricular and socio-economic areas. Trends toward new evaluating technics are to be seen in the accumulation of notes on student behavior and in the presentation of exhibits of student work. The pupil may present orally to a lay audience evidences of his work in an area of knowledge. Such methods are of great value in training for future citizenship.

A third general type of thinking is that of making selections. Imperfect selections are usually the result of a narrow, restricted point of view based on habit, emotional inhibitions, or dominance of one's own purposes or wishes. One boy felt that it would not do to study for a chemistry examination, because study only confused him.

A fourth general method of thinking is to make associations. Our schools have been erected to strengthen associative bonds. A pupil in studying may forget to see points of likeness. He may not want to see a relationship, for it jars him out of his complacency. To keep the personality intact, pupils may place the blame for failures in another quarter. A girl may think she has the qualifications for nursing, because some one has said that she looks or acts like a nurse. She may copy from others in high school, enter nurse's training, and be dismissed after a year for writing up her charts two hours in advance of the time when temperatures are to be taken.

A fifth general method of thinking is that of generalization. Pupils cannot be expected to generalize until they have recognized and defined the problem, and have clear concepts which have been dissociated from other related factors in the setting. Imperfect generalizations result through not having sufficient data, using false authorities, reasoning by analogy, and drawing hazy inferences. In reasoning by analogy the pupil may feel, because he had to collect bottles of oxygen under water, that all experiments involving the collection of gases must be done the same way. If a general impression colors an individual's judgment about a matter in all respects, his thinking will be fuzzy.

The analysis of unknown metals or non-metals is helpful in getting the pupil to reason by the method of residues or by the "process of elimination." Suppose the pupil saw an orange color in testing for an unknown metal. He would have to recall what such a result meant. If he made the correct association, he would think of calcium, but he would have to eliminate other colors and words in his thinking until the correct association was made.

The development of Boyle's Law enables a resourceful chemistry teacher to show what is meant by reasoning by the method of variable factors occurring together, or, as it is called in logic, the method of concomitant variation. If, in a series of variable causes, one cause is associated with one effect, then one may be said to be dependent on the other. The temperature being constant, Boyle found that an increase in pressure to which a given volume of gas was subjected was accompanied by a corresponding decrease in the volume of that gas, and, vice versa, that every decrease in pressure was accompanied by a corresponding increase in the gas volume. Boyle concluded that the change in volume of the gas was caused by the change in pressure.

The elements and safeguards of scientific thinking are the same for both inductive and deductive processes; only the sequences are changed. The inductive method is used primarily by the person who wants to make discoveries. This is perhaps the most difficult yet the most fruitful process for the teacher to use.

Through science clubs and classroom experiences, the pupil's attitudes must be formed and his emotions aroused before he will tackle a problem. It is doubtful if a pupil will take his place as a thinking citizen in the social order, unless he has an opportunity to practice acting on thinking in curricular and extra-curricular situations.

This means less emphasis on teacher activity and more emphasis on pupil activity. It means a teacher in the background, encouraging and building, with only occasional appearances on the center of the stage. It means working out new evaluating technics by creating organizations for the presentation of student papers, science fairs, etc.

A complete revision of our methods of teaching is in order. The subject matter of chemistry will become secondary to the scientific method. It will be clothed in more dignity as a tool, because it will be more useful and functional than ever before. Let us put away our prejudices and preconceived ideas and as true scientists help usher in this new age of chemistry.

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LETTERS

Coöperative Objective Tests in Organic Chemistry

To the Editor:

This will serve as a progress report on the work that has been done on this project, and as an invitation to others to coöperate.

As an evidence of progress, over twelve hundred tests covering the first semester's work in organic chemistry have been distributed to instructors in forty-two different institutions. In addition to this, twenty-eight other institutions have asked to be supplied with copies of these tests. This is indicative of a rather general interest in this project, and we are hopeful that something of a very definite character may be accomplished.

For the benefit of those who are not familiar with the use of objective examinations in organic chemistry, the following type test is submitted for careful consideration.

File No. *Acids, Substituted Acids, Acid Derivatives.*
Name

By encircling the proper subscripts which appear beneath each item on the left, indicate the item or items in the group listed at the right that apply with respect to:

A. THE TYPE FORMULA OR FORMULAS FOR:

1. An unsaturated monoacid — 1 2 3 4 5 6 7 8 9 10
2. A hydroxy monoacid — 1 2 3 4 5 6 7 8 9 10
3. An acid halide — 1 2 3 4 5 6 7 8 9 10

1. R·CO·OH
2. HO·OC·CH_2·CO·OH
3. $C_nH_{2n}(CO·OH)_2$
4. R·CO·X
5. R·CO·O·R
6. R·CO·O·OC·R
7. $C_nH_{2n+1}CO·OH$
8. $C_nH_{2n+1-y}(OH)_yCO·OH$
9. $C_nH_{2n-2}(CO·OH)_2$
10. Not indicated

B. THE OCCURRENCE OR OCCURRENCES OF:

4. Formic acid — 1 2 3 4 5 6 7 8 9 10
5. Maleic acid — 1 2 3 4 5 6 7 8 9 10
6. Octyl acetate — 1 2 3 4 5 6 7 8 9 10

1. Rhubarb
2. Ants
3. Berries
4. Oranges
5. Peppermint
6. Rancid butter
7. Tobacco
8. Nettles
9. Carrots
10. Animal tissue

C. THE USE OR USES OF:

7. Stearic acid — 1 2 3 4 5 6 7 8 9 10
8. Lactic acid — 1 2 3 4 5 6 7 8 9 10
9. Sodium palmitate — 1 2 3 4 5 6 7 8 9 10

1. In infant foods
2. As a soap
3. In cosmetic creams
4. As a solvent
5. In baking powders
6. To remove iron rust
7. In shoe polish
8. In perfumes
9. In soft drinks
10. No use indicated

D. THE NAME OR NAMES OF:

10. HO·OC·CH_2·CO·OH — 1 2 3 4 5 6 7 8 9 10
11. CH_3·CHOH·CO·OH — 1 2 3 4 5 6 7 8 9 10
12. CH_3·CH_2·CO·O·CH_3 — 1 2 3 4 5 6 7 8 9 10

1. Malonic acid
2. Propanedioic acid
3. Methyl acetate
4. Lactic acid
5. Pyruvic acid
6. Succinic acid
7. 2-Hydroxypropanoic acid
8. Glutaric acid
9. Methyl ethanoate
10. Name not indicated

E. THE REAGENT OR REAGENTS REQUIRED FOR:

13. $CH_3·CN \longrightarrow CH_3·CO·OH$ — 1 2 3 4 5 6 7 8 9 10
14. $H_2N·CH_2·CO·OH \longrightarrow HOCH_2·COOH$ — 1 2 3 4 5 6 7 8 9 10
15. $CH_3·CO·OH \longrightarrow CH_3CO·O·OCCH_3$ — 1 2 3 4 5 6 7 8 9 10

1. Distilled water
2. HONO/($NaNO_2$/H^+), aq.
3. Heat
4. $H_2C:C:O$
5. Distil
6. NaOH, aq., heat
7. $2H_2O/H^+$
8. PCl_5
9. $CH_3·CO·OH/(P_2O_5)$
10. Not indicated here

F. THE REAGENT REQUIRED FOR EACH STEP IN:

16. $CH_3·CO·OH \longrightarrow a$ — 1 2 3 4 5 6 7 8 9 10
17. $a \longrightarrow b$ — 1 2 3 4 5 6 7 8 9 10
18. $B \longrightarrow HO·OC·CH_2·CO·OH$ — 1 2 3 4 5 6 7 8 9 10

1. HCl, dry
2. Cl_2/(S, light)
3. Cl_2, aq.
4. H·CN/(NH_3)
5. $H_2Cr_2O_7$, aq., heat
6. Na·CN
7. Na/CH_3·CH_2·OH
8. $2H_2O/H^+$
9. Air/$(AcO)_2Mn$
10. Not indicated here

G. THE DESCRIPTION OR DESCRIPTIONS THAT APPLY:

19. CH_3·CO·OH — 1 2 3 4 5 6 7 8 9 10
20. CH_3·CHOH·CO·OH — 1 2 3 4 5 6 7 8 9 10
21. CH_3·CO·O·CH_2·CH_3 — 1 2 3 4 5 6 7 8 9 10

1. Colorless liquid
2. Pleasant odor
3. Irritating odor
4. Water soluble
5. Sweet taste
6. Ether soluble
7. Sour taste
8. Brown color
9. Insoluble in water
10. Viscous

H. THE PRODUCT OR PRODUCTS FORMED BY:

22.	$C_6H_6 + air/(V_2O_5, 450°C.) \longrightarrow$	1. Succinic anhydride	6. Maleic anhydride
23.	$CH_3{\cdot}CHO + H{\cdot}CN + 2H_2O/H^+ \longrightarrow$	2. Oxalic acid	7. $NaO{\cdot}OC{\cdot}CO{\cdot}ONa$
24.	$2H{\cdot}CO{\cdot}ONa + heat, 200°C. \longrightarrow$	3. Lactic acid	8. $NC{\cdot}CH_2{\cdot}CHO + H_2$
		4. $NaOH + CaO$	9. $CH_3{\cdot}CHOH{\cdot}CO{\cdot}OH$
		5. $HO{\cdot}OC{\cdot}CO{\cdot}OH$	10. Not indicated here

I. TYPE REACTION OR REACTIONS FOR:

25.	$CH_3{\cdot}CO{\cdot}OH$	1. Polymerization	6. Halogenation/catalyst
26.	$CH_3{\cdot}CHOH{\cdot}CO{\cdot}OH$	2. Burning, vapor phase	7. Reduction/catalyst
27.	$CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$	3. Oxidation, mild	8. Addition
		4. Lactide formation	9. Alcoholysis
		5. Saponification	10. Ammonolysis

J. THE REAGENT OR REAGENTS THAT REACT READILY WITH:

28.	$CH_3{\cdot}CH_2{\cdot}CO{\cdot}OH$	1. NaOH, aq.	6. NH_3, aq.
29.	$HOOC{\cdot}CHOH{\cdot}CHOH{\cdot}COOH$	2. PCl_5	7. $Cu^{++}/(OH^-)$, aq.
30.	$CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	3. $CH_3{\cdot}CH_2{\cdot}OH/H^+$	8. $CH_2{\cdot}CO{\cdot}Cl$
		4. Na	9. $NaHCO_3$, heat
		5. Superheated steam	10. $NaOH/(CaO)$, heat

K. THE REAGENT OR REAGENTS THAT WILL AID IN IDENTIFYING:

31.	$HO{\cdot}OC{\cdot}CO{\cdot}OH$	1. c. H_2SO_4, heat	6. $Ca(OH)_2$, aq.
32.	$HOOC{\cdot}CHOH{\cdot}CHOH{\cdot}COOH$	2. $KMnO_4/H^+$, aq., heat	7. $CH_3{\cdot}CH_2{\cdot}OH$
33.	$CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3$	3. Cu^{++}/OH^-, aq.	8. Heat
		4. C_6H_6	9. Distil (b. p.)
		5. c. NH_3/H_2O, stand, distil	10. Not indicated here

L. THE COMMERCIAL SYNTHESIS OR SYNTHESES OF:

34.	$CH_3{\cdot}CHOH{\cdot}CO{\cdot}OH$	1. $CH_3{\cdot}CHO + HCN + 2H_2O/H^+ \longrightarrow$
35.	$CH_3{\cdot}CO{\cdot}OH$	2. $C_2H_2 + H_2O/(Hg^{++}, H_2SO_4) + air/(AcO)_2Mn \longrightarrow$
36.	$CH_3{\cdot}CO{\cdot}O{\cdot}OC{\cdot}CH_3$	3. $C_6H_6 + air/(V_2O_5, 450°C.) + H_2O \longrightarrow$
37.	$H{\cdot}CO{\cdot}OH$	4. $CH_3{\cdot}CO{\cdot}Cl + Na{\cdot}O{\cdot}CH_2{\cdot}CH_3 \longrightarrow$
38.	Maleic acid	5. $CH_3{\cdot}CO{\cdot}OH + H_2C{:}C{:}O \longrightarrow$
39.	$CH_3{\cdot}OH$	6. $CO + NaOH, 200°C. + H^+, aq. \longrightarrow$
40.	$CH_3{\cdot}CH_2{\cdot}OH$	7. $C_2H_2 + 2CH_3{\cdot}CO{\cdot}OH/(catalyst) + heat \longrightarrow$
		8. $CH_3{\cdot}CH_2{\cdot}CO{\cdot}OH + Cl_2/(S) + NaOH, aq. + H^+, aq. \longrightarrow$
		9. $CH_3{\cdot}CO{\cdot}O{\cdot}OC{\cdot}CH_3 + H_2O/H^+ \longrightarrow$
		10. $H{\cdot}CHO + H_2/(catalyst) \longrightarrow$
		11. $H_2C{:}CH_2 + H_2SO_4 + H_2O$, distil $\longrightarrow$
		12. $CO + H_2/(catalyst)$, heat, pressure $\longrightarrow$

This examination, in the opinion of the writer, satisfies all of the normal requirements of a test as a measuring device. Twelve different approaches to a tapping of the student's knowledge are utilized, each of which may be rated according to its relative importance with respect to the topic covered. The diversity of choices, under each of the general divisions, practically eliminates guessing. Guessing, in an examination of this type, is especially disconcerting to the student if the test is rated on the basis of right minus wrong.

A careful consideration of this test will indicate that it is not an examination in which the student returns, in a parrot-like manner, what he has heard in the classroom or read in his book. The organization is different, and a set of thought-provoking possibilities present themselves. The student is required to think, and think accurately. The "spoon-fed student" becomes lost in a maze of uncertainties.

A slight modification of this test, in which a special answer sheet is used, makes it possible to rate this type of test by the new automatic grading machines that are now available in certain institutions. In one such test, two hundred thirty papers were accurately scaled on the basis of right minus wrong in just seventy-eight minutes. Since there were ninety-six items on each paper, this meant grading twenty-two thousand eighty items. What an economy of time and energy on the part of the instructor that may now be expended in the form of more constructive work!

Any who are interested in coöperating on this project should contact the writer.

E. F. DEGERING

PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

The Hare and the Horse

To the Editor:

It is not inevitably obvious that HI means one part (0.8 per cent) of hydrogen and 127 parts (99.2 per cent) of iodine, and not one part of hydrogen and one part of iodine. Hence the suitability of the Fable of the Hare and the Horse.

Once upon a time a voyager in a far land desired rabbit stew. When it arrived he demanded if it contained horse meat. "But yes," replied the garçon, "half-and-half, one rabbit and one horse."

E. A. VUILLEUMIER

DICKINSON COLLEGE
CARLISLE, PENNSYLVANIA

Out of the Editor's Basket

AT THE Detroit meeting of the A. C. S. a paper was read before the Division of Chemical Education by H. E. Bent and C. L. French on "Ferric Thiocyanate and Related Equilibria." The technical details of the research, published elsewhere, are of no immediate concern, but since this reaction is so commonly used in lecture demonstrations the results should be called to attention.

They have shown that the red-colored substance is a positive complex ion, $FeCNS^{++}$. Their own comment on this is:

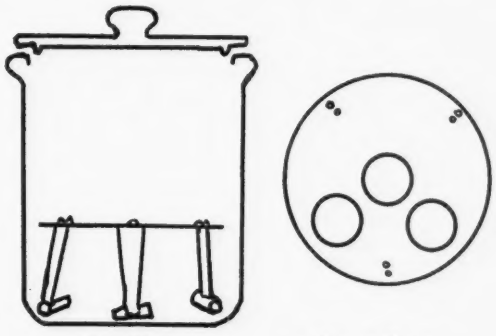
"The significance of these results for teachers of general chemistry is perhaps too obvious to require comment. The formation of a red color with the addition of thiocyanate to ferric ion is too beautiful an example of equilibrium to be discarded and may still be used. The incompleteness of the reaction makes it an excellent illustration of the way in which a reaction may be forced more nearly to completion by the addition of either of the reactants. The only change required to bring former discussions of this reaction in harmony with these experiments is to leave off the subscript on the thiocyanate.

"On the other hand this reaction can *not* be used to show the reversal of an equilibrium by the addition of one of the products of the reaction. Since this reaction is fundamentally one of addition and not one of interchange there is no other product to add in order to demonstrate reversal of the reaction. The time-honored addition of ammonium chloride, or for that matter any other of a dozen of salts to reverse the reaction probably involves an explanation which is too involved for the average course in general chemistry. As has been shown by DuBois the effect of salts on this equilibrium is to be attributed to the decrease in activity of the reactants as compared with the product of the reaction as a result of the increase in ionic strength. This explanation was advanced when it was assumed that the colored complex was a negative ion, but is also applicable to the case of a positive ion. Since the reaction takes place with a decrease in the sum of the squares of the charges on the ions an increase in the ionic strength will reverse the reaction."

● L. L. Woods, of St. Augustine's College, Raleigh, North Carolina, had occasion to investigate the literature on properties and uses of tellurium, and since there is very little common information about the element we thought it worth while to mention some of the interesting facts about it.

It has some uses in ceramics; fused with soda glass it yields colors from red to blue. Its vapor is said to be fluorescent. It has some use in lead alloys. Among its physiological properties and medical uses are the following: In a test for diphtheria, the throat, when swabbed with dilute potassium tellurite, turns black if infected. Potassium tellurite, in agar, is used in the isolation of pneumococci. Injections of tellurium or its salts, suspended in oil or in glucose solutions, are said to arrest the development of leprosy. Its pharmacological properties are similar to those of arsenic. It is less toxic than selenium, due, perhaps, to its easier reduction to the element. The garlic-like odor which it imparts to the breath is traceable to $(CH_3)_2Te$, which can be detected in amounts as small as half a microgram. Work with the element is disagreeable because of the body odors it produces.

● The accompanying illustration shows how F. Cassaretto, of Loyola University, Chicago, was able to make cheap but serviceable desiccators out of cookie jars obtained from the five- and ten-cent store. The tray is sheet aluminum and the legs are held firmly wedged into the bottom of the jar by inserting them into rubber stoppers. The covers are ground with coarse carborundum powder to fit the tops of the jars.



SIDE VIEW TOP OF TRAY

● Apropos of "mnemonic devices,"[1] B. B. Banks, of Mary Allen Junior College, Crockett, Texas, sends in the following one to jog the memories of those who are confused about litmus colors:

R	BASE
E	L
ACID	U
	E

● "Bigger and better atom-smashers" seems to be the slogan of the day. The General Electric Company has announced receipt of an order for the electrical equipment for a new 100,000,000-volt cyclotron at the University of California, which engineers say will be so powerful that its ion-beam will melt an ordinary brick as easily as a blowtorch does a pound of butter. Energies to be attained are greater than those found anywhere except in some of the distant stars.

● Despite the difficulties, it seems that the JOURNAL is being delivered in Germany with some regularity. One of our contributors reports a request from Dresden for a reprint of a recent article and he wonders if others have had any similar foreign contacts lately.

[1] J. CHEM. EDUC., **16**, 516 (1939); **17**, 338, 545, (1940).

● At a recent meeting of the Midwest Section of the American Association of Cereal Chemists Mr. Albert I. Kegan, chemist and lawyer, spoke on the Food, Drug, and Cosmetic Law and the Wheeler-Lea amendment to the Federal Trade Commission Act. We think some of his observations may be worth repeating here. He pointed out that if a drug manufacturer wishes to put a new product on the market in interstate commerce, it is necessary for him to obtain permission from the Government before doing so. In order to obtain that permission he must submit sample and complete specification of the product. It was Mr. Kegan's opinion that the time may come when the same procedure will apply when new types of food are introduced. The Food and Drug Law goes a long way toward increasing the control of private business by government and it was Mr. Kegan's opinion that the trend will increase in that direction in the coming years.

RECENT BOOKS

ORGANIC REAGENTS USED IN QUANTITATIVE INORGANIC ANALYSIS. *W. Prodinger*, Ph.D. Translated by *S. Holmes* from the second German edition. First Edition. Nordemann Publishing Co , Inc., New York City, 1940. xiv + 203 pp. 4 figs. 15 × 23 cm. $5.00.

The author's stated purpose in writing this book is to survey the most important organic precipitants with the view of collecting and interpreting them in such a manner that they can be used and developed by the practical analyst. Because the already voluminous and rapidly increasing literature of organic precipitants is widely scattered, with much of it in foreign journals, and often is not directly applicable to analytical problems, a book of this type fills a real need. The reviewer feels that the author has largely accomplished his purpose; this is attested by the fact that a second German edition followed the first in less than two years. The translator has remedied a deficiency in the German text by including sections on Oxine and Neocupferron. The first few pages of the book deal briefly with the pertinent theory of the analytically important types of complex compounds. The next twenty pages contain discussion of the theory and general applications of some seventeen typical organic precipitants. The remainder of the book gives detailed directions for the use of some twenty-five organic precipitants for quantitative separations and determinations on a macro and, when practicable, on a micro scale. This book should find a place in every analytical library.

W. W. RUSSELL

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

PHYSICAL CONSTANTS OF HYDROCARBONS. *G. Egloff*. Reinhold Publishing Corporation, New York City, 1939. 403 pp. 15 × 23 cm. $9.00.

"The collating and critical evaluation of physical constants of hydrocarbons is of recognized importance to all workers in hydrocarbon chemistry. With the tremendous increase in this field of research during the past fifteen years the customary sources of physical constant data have become inadequate due to more precise developments in synthesis, purification, and methods of determining physical constants. The experimental data of recent years lend themselves to more significant analyses. Hence, a greater reliability can be attributed to relationships between the different homologous series of hydrocarbons which show the dependence of physical properties upon their structure. In the present work, the critical study of the hydrocarbon constants and their interrelationships to derive useful and sound generalizations has been the desired goal."

BRITISH CHEMICALS AND THEIR MANUFACTURERS: THE OFFICIAL DIRECTORY OF THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. Association of British Chemical Manufacturers, 166 Piccadilly, London, W. 1, England, 1939. 487 pp. 13.5 × 21.5 cm.

This book is obtainable gratis by inquirers who are genuine purchasers of chemicals. Copies are only issued from the office of the Association to such inquirers.

CHEMISTRY TESTS. *Kenneth E. Conn*, Bloomington High School, Bloomington, Indiana, and *Herman T. Briscoe*, Indiana University, Bloomington, Indiana. Mentzer, Bush and Co., New York City, 1939. 19 × 25.5 cm. 62 pp. (Forms A and B). Each form may be secured for $0.15 net.

These tests were prepared for use with the authors' COMBINED LABORATORY MANUAL AND WORKBOOK IN CHEMISTRY, but they may be used with other texts or workbooks, which deal with chemistry at the secondary-school level, and which are organized on the same general plan as the authors' book.

It is difficult to evaluate these tests in terms of their general usefulness in high-school chemistry. The authors consider them adequate for use with their COMBINED LABORATORY MANUAL AND WORKBOOK IN CHEMISTRY. The units have been carefully prepared, and they deal adequately and well with the descriptive aspects of high-school chemistry, except in a few cases where the answers expected are too obvious, and in a few others where the correct answer is not to be found among the four answers offered. Many teachers believe that the quantitative aspects of chemistry are very important, even at the high-school level. These teachers will not consider the Conn and Briscoe tests adequate, because of the dearth of numerical problems offered.

J. O. FRANK

WISCONSIN STATE TEACHERS COLLEGE
OSHKOSH, WISCONSIN

CALCULATIONS OF QUALITATIVE ANALYSIS. *L. J. Curtman*, Professor of Chemistry, and *S. M. Edmonds*, Instructor in Chemistry, The College of the City of New York. The Macmillan Company, New York City, 1940. vii + 156 pp. 2 figs. 15 × 23.5 cm. $2.00.

This text contains several hundred numerical problems which, for the most part, deal with ionic equilibrium. The topics included in the text are as follows: (1) General Properties of Strong and Weak Electrolytes, (2) Chemical Equations, (3) Chemical Formulae and Equations, (4) Solutions, (5) Non-Redox and Redox Reactions, (6) Chemical Equilibrium and Ionization, (7) Solubility Product, (8) The Ionization of Water—Oxonium Ion Concentration, (9) Complex Ions, (10) Theory of Redox Reactions.

The text is designed to accompany laboratory procedures of qualitative analysis or to supplement other texts in the subject which do not stress the numerical calculations. In each chapter there is given a brief discussion of the theory pertaining to the type of calculation involved. In some cases this discussion is equivalent to what is usually found in the standard textbook of qualitative analysis. Although in most chapters the descriptive material is sufficient to enable the student to solve the problems, the book is not to be regarded as complete for a course in qualitative analysis. The appendix contains a section on mathematical operations which the student will find very useful. Tables of ionization and dissociation constants appear throughout. Teachers of qualitative analysis will welcome a text of this type to supplement their courses in the field.

WARREN C. JOHNSON

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

ESSENTIALS OF NUTRITION. *H. C. Sherman* and *C. S. Lanford*, Columbia University. First Edition. The Macmillan Company, New York City, 1940. x + 418 pp. 34 figs. 10 × 17 cm. $3.50.

The purpose of this book is to "offer its readers a thoroughly adequate and up-to-date view of the essentials of nutrition." The book is written for the reader who has had no previous training in science. Anyone who has endeavored to interpret biochemical research for lay audiences will appreciate the admirable manner in which the authors have handled this difficult task. Chemical formulas and complex chemical definitions and explanations are conspicuous by their absence.

The book, which evidently is designed for the freshman college student, contains 21 chapters covering most of the usual topics of interest to students of nutrition. These are treated, however, from the viewpoint of practical application. A few representative chapters are as follows: I. The Nutritional Improvement of Life; V. How to Meet the Energy Need and Have the Body Weight You Want; VI. How to Meet the Need for Protein; XI. Food Costs and Food Values; XXI. How to Make Nutritional Knowledge More Effective, etc. Each chapter is followed by thought-provoking "exercises" and "suggested readings." In the opinion of the reviewer, most of the latter cannot be read to advantage by the type of reader for which the book is intended. Other chapters deal with the essential facts of digestion, food composition, function of food ingredients, mineral elements, vitamins, etc. Naturally, discussions of metabolic changes are omitted.

The appendix is divided into five parts giving, in greater detail, information to supplement the text. An adequate subject index comprises the last 15 pages.

The reviewer feels that the discussion of statistical methods could be omitted without detracting from the use of the book. The style is simple and understandable and will appeal to those who have had no formal scientific training; the book should be in every high-school library. It is the hope of the reviewer, however, that college teachers will not be tempted to use this excellent book as an excuse for even less formal chemical training of college students who are contemplating a college course in nutrition.

R. ADAMS DUTCHER

PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

COLLECTED PAPERS OF WALLACE HUME CAROTHERS ON HIGH POLYMERIC SUBSTANCES. Edited by *H. Mark*, Adjunct Professor of Organic Chemistry, Brooklyn Polytechnic Institute, and *G. S. Whitby*, Director of Chemical Research, Chemical Research Laboratory, Teddington, Middlesex. Interscience Publishers, Inc., New York City, 1940. xix + 459 pp. 35 figs. 15 × 23 cm. $8.50.

This is the first volume of a series on high polymers, and contains the fifty-three papers published on this subject by the late Dr. Carothers. They are divided into three sections: (1) Studies on polymerization and ring formation, (2) Acetylene polymers and their derivatives, and (3) Miscellaneous papers on polymerization.

There are very good introductions to each section, a biographical sketch by Roger Adams, a complete bibliography including a list of Carothers' fifty-two patents, and excellent author and subject indexes.

As stated in the introduction, "No investigator has excelled Wallace Hume Carothers in advancing our knowledge of high polymeric chemistry and at the same time providing a basis for the development of technically useful synthetic polymeric materials." The interesting synthetic rubber neoprene, and the intriguing synthetic fiber nylon are products for which he laid the theoretical and experimental foundation.

The book is well printed and is apparently free from typographical errors.

HARRY L. FISHER

U. S. INDUSTRIAL CHEMICALS, INC.
STAMFORD, CONNECTICUT

THE INTERVIEW METHOD OF TEACHING QUALITATIVE ANALYSIS. *A. M. Ewing*, Texas Wesleyan College. The Author, Fort Worth, Texas, 1940. 52 pp. 20 × 27.5 cm. $1.00.

The contents of this paper-covered pamphlet may be summarized as follows: 5 pages of introduction, definitions and general directions; 11.5 pages of procedures for the analysis of common metals; 11.5 pages of diagrams of the schemes, with beakers, funnels, and evaporating dishes used to show the operations involved; 2 pages of tests covering 19 acid radicals; 8 pages devoted to 10 topics in general theory; 2 pages of tables of solubility, bead tests, flame tests, and common valences; and 10 pages of students' record sheets for analyses of unknowns.

The pamphlet is intended to provide a very simple introduction to qualitative analysis as the laboratory work for the latter part of the first year's course in chemistry. The ground covered is too extensive, however, to permit proper detail for many of the procedures; furthermore, attention is directed almost wholly to the use of reagents to obtain separations and tests, with considerable disregard of the reactions involved. The main novelty of treatment, aside from the diagrams, may be seen in the following quotation: "Why use HCl in the precipitation of Group One? The chlorides of Pb, Ag, Hg are insoluble in water and dilute solutions of strong acids, and therefore precipitate and can be filtered."

There are several good ideas in the pamphlet, but they are not all worked out with sufficient care and accuracy to permit unqualified recommendation. The intelligent student would need to consult other books for many of the reactions as well as for additional details of technic. In doing so he might easily uncover a sufficient number of mistakes to cause him to lose confidence in the pamphlet itself.

R. K. MCALPINE

UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

AN INTRODUCTION TO ORGANIC CHEMISTRY. *A. Lowy*, Ph.D., Professor of Organic Chemistry, University of Pittsburgh, and *B. Harrow*, Ph.D., Professor of Chemistry, College of the City of New York. Fifth Edition. John Wiley and Sons, Inc., New York City, 1940. xv + 400 pp. 15 × 23 cm. $3.00.

The authors and publishers of this text, in conformity with previous practice, have again produced a new revised edition after four years. This work is designed for a two-semester (two hours a week) course. It contains well-recognized basic principles of organic chemistry, as well as recent and important applications, the whole being woven together into a simple and readable narrative.

All of the essential features of previous editions have been retained and many new innovations have been added. Smaller type has been used for most formulas and equations, conserving considerable space yet retaining the former attractive appearance. The addition of "questions" at the end of each chapter is a decided improvement. One page of molecular models has been included. The last chapter again deals with nomenclature of organic compounds and a rather extensive system for group and ring systems has been added. The two chapters on carbohydrates, enzymes, vitamins, and hormones have been completely revised. However, no mention is made of the furanose form of glucose. Considerable new material has been added, including the formulas of vitamins E and K. Three new charts have been incorporated and one deleted. Six new or additional portraits have been included. The appendix contains new tables on dissociation constants of acids and Latin and Greek roots in chemical terminology. All references at the ends of the several chapters have been omitted but the bibliography at the end of the book has been revised to include many new and recent volumes. Recent work on the vapor phase nitration of aliphatic hydrocarbons is mentioned.

Fundamentally it is a case of a good book made better. It should continue to retain a place of importance among organic texts for survey and service courses.

RALPH E. DUNBAR

NORTH DAKOTA AGRICULTURAL COLLEGE
FARGO, NORTH DAKOTA

MICRO-DIFFUSION ANALYSIS AND VOLUMETRIC ERROR. *E. J. Conway*, M.B., D.Sc., Professor of Biochemistry, University College, Dublin. D. Van Nostrand Co., Inc., New York City, 1940. xiii + 306 pp. 51 figs. 14 × 22 cm. $6.00.

This useful book describes procedures developed by the author and others for the determination of small quantities of ammonia, urea, adenylpyrophosphoric acid, adenylic acid, adenosine, volatile amines, chlorides, bromides, CO_2, acetone, and alcohol. The "Conway Unit" is used in all of these determinations. This unit consists of a pyrex glass container resembling a small Petri dish with thick glass walls, within which a second chamber is formed by a circular wall of glass arising from the floor. The wall of the inner chamber is about one-half the height of the outer. The sample to be analyzed is placed in the outer chamber and the volatile substances arising therefrom are absorbed by means of appropriate reagents in the inner chamber. By this means, extremely small quantities can be analyzed with an accuracy comparing favorably with that of macro methods.

Students and biochemists will find the discussion of the design and use of micro glassware very helpful. The accuracy of micro methods is limited largely by the accuracy of measurement of the sample and volumetric reagents and by the limitations inherent in the chemical reactions involved in the determinations. The author discusses fully the many sources of error and gives methods for their evaluation.

THEODORE E. FRIEDEMANN
NORTHWESTERN UNIVERSITY MEDICAL SCHOOL
CHICAGO, ILLINOIS

SCIENCE FOR THE WORLD OF TOMORROW. *G. Wendt*, Director, Department of Science, New York World's Fair. W. W. Norton and Co., New York City, 1939. xvii + 300 pp. 70 figs. 15 × 23 cm. $2.75.

There is no reader, whether he be a scientist, teacher, or layman, who will not be fascinated by certain descriptions which the author has written in this commentary. With some material, Wendt appears to have a knowledge, understanding, and comprehension that allows him to do a most commendable and masterful piece of work. His chapter, entitled, "Three Times a Day," in which he discusses foodstuffs, is excellently written as are also the units in which he tells something of the new synthetic wearing apparel, new household uses for synthetics, the new fluorescent lights, as well as the discussion dealing with the effect of science on the age expectancy of man. He has given a huge number of statistical figures, many of which are both interesting and startling. However, they often stand out indelibly as if they had been contained in the original outline and therefore must be inserted some place under the various headings to which each has been assigned.

This reviewer is impressed by the observation that a similar book might have been written almost as successfully by an intelligent observer with little knowledge, but with a huge notebook. There is no one who would not be interested in straightforward information from such a notebook, for it would prove very illuminating. However, this same information becomes burdensome to read when it is put into sentence and paragraph form with artificial or poorly chosen thoughts connecting them. The book would undoubtedly have been of interest to many more readers if the material had been presented as pure facts and direct observations. This would still have allowed the author to inject real contributory facts wherever he could and saw fit. It should be added that much of this actual content is the type that might advantageously find its way into a comprehensive guidebook to the World's Fair, and this reviewer does not wish to intimate that the material chosen is not interesting content for a book. The fact remains, however, that, for the reader who can scan through a book and select the important items from the insignificant, this book will prove valuable, but for those who try to read somewhat thoroughly from paragraph to paragraph, the book will have only its first few pages turned.

SHAILER A. PETERSON
UNIVERSITY HIGH SCHOOL
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

AN INTRODUCTION TO BIOCHEMISTRY. *W. R. Fearon*, M.A., Sc.D., M.B., F.I.C.; Fellow of Trinity College, Dublin; Member of the Royal Irish Academy. Second Edition. The C. V. Mosby Company, St. Louis, Mo., 1940. xii + 475 pp. 14 × 21.5 cm. $3.75.

The small size of this book is deceptive, for a great deal of sound and up-to-date science is included between its covers. Well chosen lists of reviews and monographs for further reading are appended to most of the twenty-five chapters. An unusual feature is the presentation of laboratory directions, mostly for qualitative tests, scattered at various points throughout the book. Detailed treatment of the chemistry of tissues has been avoided, and the order in which substances are discussed is based, for the most part, on their chemical rather than physiological classification.

Teachers of medical students are likely to prefer larger texts which relate the subject more closely to physiological and medical problems. This book should be particularly useful in those courses in which biochemistry is treated as an independent science.

DAVID I. HITCHCOCK
YALE UNIVERSITY SCHOOL OF MEDICINE
NEW HAVEN, CONNECTICUT

CHEMISTRY IN THE SERVICE OF MAN. *A. Findlay*, Professor of Chemistry, University of Aberdeen, Scotland. Fifth Edition. Longmans, Green and Co., London, 1939. xx + 398 pp. 74 figs. 12 × 18.5 cm. $2.50.

The fifth edition of Professor Findlay's popular book on the useful services of chemistry retains all the fine features of former editions. An additional chapter (XVII) on Vitamins and Hormones is solidly linked to the text, and the entire content has been brought into tune with modern developments. Interesting high-lights include discussions of explosives, fertilizers, glass, and plastics.

The book is designed for the non-technical reader. If, however, the reader has at some time studied elementary chemistry, the book will be the more valuable. Its worth as a follow-up text for lay readers is obvious. In addition, secondary schools will welcome it as a modern reference work. As a textbook in college survey courses it fills a need for a readily assimilated book *about* chemistry; it is not, however, for the training of chemists.

ELBERT C. WEAVER
BULKELEY HIGH SCHOOL
HARTFORD, CONNECTICUT

THE CHEMICAL CONSTITUTION OF NATURAL FATS. *T. P. Hilditch*, D.Sc. (Lond.), F.I.C., Campbell Brown Professor of Industrial Chemistry in the University of Liverpool. First Edition. John Wiley and Sons, Inc., New York City, 1940. xi + 438 pp. 8 figs. 15 × 24.5 cm. $6.50.

This book gives an account of the constitution of fats which are produced naturally in plant and animal life. The term "fat" is used in the restricted sense and refers to the natural triglycerides. After an introductory chapter covering a survey of the natural fats, the author takes up a systematic description beginning with the component acids of the fats of minute aquatic flora and fauna, going on to those of the larger aquatic invertebrates, and then to those of land animals and vegetables. As far as possible the concentrations of the respective component acids are discussed quantitatively, and there are numerous useful tables interspersed. The component glycerides of the above fats are taken up next. The concluding chapters of the book discuss the biochemistry of fats, constitution of individual natural fatty acids, synthetic glycerides, and notes on experimental technic employed in the quantitative estimation of fats. The book is well written, remarkably free from errors, and covers the field most extensively. It should be of value to the chemical technologist, the biochemist, and research workers in the field of fats and related subjects.

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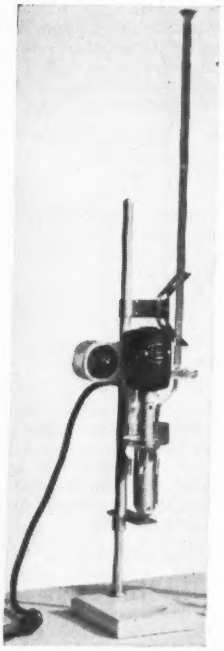

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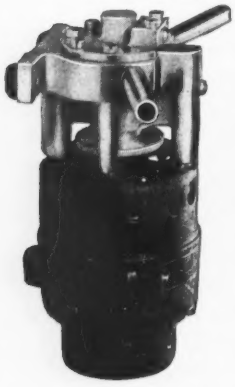

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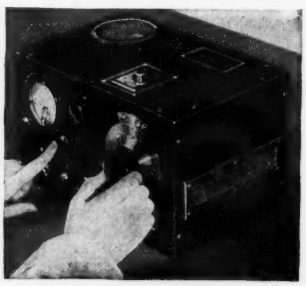

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